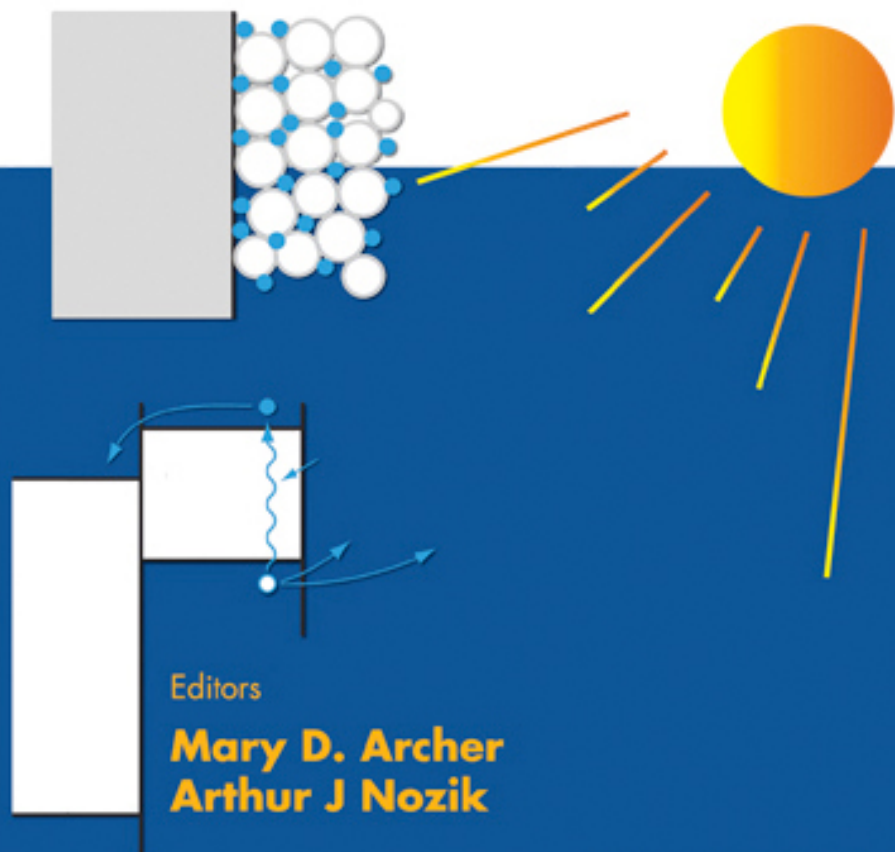


NANOSTRUCTURED AND PHOTOELECTROCHEMICAL SYSTEMS FOR SOLAR PHOTON CONVERSION



Imperial College Press

**NANOSTRUCTURED AND
PHOTOELECTROCHEMICAL
SYSTEMS FOR
SOLAR PHOTON CONVERSION**

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NANOSTRUCTURED AND PHOTOELECTROCHEMICAL SYSTEMS FOR SOLAR PHOTON CONVERSION

Editors

Mary D. Archer

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This volume is dedicated

to

Olga I. Mićić

21 December 21 1934 – 24 May 2006

a fine scientist and pioneer in the field of quantum dots

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Mary Archer read chemistry at Oxford University and took her PhD from Imperial College, London, in 1968. From 1968 to 1972, she did post-doctoral work in electrochemistry with Dr John Albery at Oxford, and she then spent four years at The Royal Institution in London, working with Lord Porter (then Sir George Porter) on photoelectrochemical methods of solar energy conversion. She taught chemistry at Cambridge University from 1976 to 1986. From 1991 to 1999, she was a Visiting Professor in the Department of Biochemistry at Imperial College, London, and from 1999 to 2002, she held a Visiting Professorship at ICCEPT (Imperial College Centre for Energy Policy and Technology). She is President of the UK Solar Energy Society and the National Energy Foundation and a Companion of the Energy Institute. She was awarded the Melchett Medal of the Energy Institute in 2002 and the Eva Philbin Award of the Institute of Chemistry of Ireland in 2007.

Jessica Benson-Smith was awarded the British Marshall Scholarship in 2004. As a recipient of this fellowship, she became a postgraduate student in the Experimental Solid State Physics Department at Imperial College, London, from which she received her PhD in 2007. She specialises in the spectroscopy of organic bulk heterojunction films for organic solar cell applications.

James Durrant is Professor of Photochemistry in the Department of Chemistry at Imperial College, London. After completing his undergraduate studies in physics at the University of Cambridge, he obtained a PhD in biochemistry at Imperial College, London, in 1991, studying the primary reactions of plant photosynthesis. After postdoctoral positions and a BBSRC Advanced Fellowship, he joined the Chemistry Department at Imperial College in 1999. His interests are in photochemical approaches to solar energy conversion, electron-transfer dynamics and excitonic solar cells.

Alexei Emeline obtained his MSc in Physical Chemistry from Tomsk State University in 1990 and his PhD in Molecular Physics from St Petersburg State University in 1995. He started his academic research career at St Petersburg State University as a researcher at the V. A. Fock Institute of Physics in 1995, and later in the same year as an assistant professor of the Faculty of Physics. In 1996 he was awarded a NATO Science Fellowship to take up a post-doctoral fellowship at Concordia University in Canada under the supervision of Professor Nick Serpone. From 1998 to 2004, he remained in the same laboratory at Concordia University as an associate researcher. In 2005 he was awarded a JSPS Fellowship and spent one year in the group of Professor Akira Fujishima at Kanagawa Academy of Science and Technology in Japan. He is currently a senior researcher, working for his DSc in the V. A. Fock Institute of Physics of St Petersburg State University. His research interests focus on fundamental studies of interfacial photophysical and photochemical processes in heterogeneous systems, particularly on the role of photoexcitation conditions on the direction and efficiency of different photoprocesses.

Anthony Fitch received his undergraduate degree at the University of Nebraska at Kearney and is currently pursuing his PhD at Caltech under the advisement of Nathan S. Lewis.

Michael Grätzel is a professor at the École Polytechnique de Lausanne, where he directs the Laboratory of Photonics and Interfaces. He discovered a new type of solar cell based on dye-sensitised mesoscopic oxide particles and pioneered the use of nanocrystalline materials in electroluminescent and electrochromic displays, as well as lithium ion batteries and bioelectronic sensors. Author of over 500 publications, two books and inventor of more than 50 patents, his work has received over 40,000 citations so far, ranking him amongst the most highly-cited scientists worldwide. He has received several prestigious awards, including the Faraday Medal of the (British) Royal Society of Chemistry, the Dutch Havinga award, the Italgas prize, the European

Millennium award for Innovation, the 2006 World Technology Award in Materials and the Gerischer award. In 2006, he was selected by Scientific American as one of the fifty top researchers in the world. He received his doctor's degree in Natural Science from the Technical University, Berlin, and holds honorary doctorates from the Universities of Delft, Uppsala and Turin. He is a member of the Swiss Chemical Society and the European Academy of Science and an elected honorary member of the Société Vaudoise de Sciences Naturelles.

Gary Hodes received his BSc and PhD from Queen's University of Belfast in 1968 and 1971 respectively, and has been at the Weizmann Institute of Science, Rehovot, Israel since 1972. His research has focused on semiconductor film deposition from solutions (initially electrochemical and later chemical bath deposition) and on various types of solar cells (liquid junction, thin film, polycrystalline and nanoporous) and quantum dots using these films. Throughout his career, he has also studied various aspects of semiconductor surface treatments. More recently, he is continuing work on various aspects of chemical bath deposition mechanisms and also increasingly concentrating on nanocrystalline, semiconductor-sensitised solar cells.

Rolf Könenkamp is the Gertrude-Rempfer Professor of Physics at Portland State University in Portland, Oregon. His present research interests lie in the field of nanoscience. He has worked extensively on semiconductor devices, such as nanostructured solar cells and nanowire light-emitting diodes and transistors, and he holds several patents in this area. He has led the design and construction of a new high-resolution photoelectron microscope since 2002. This will be one of the first aberration-corrected microscopes of this type and it will be used to explore transport and confinement effects on the nanoscale. He has worked at NREL, HMI Berlin, Hitachi Tokyo, Princeton University and at the IST in Lisbon, and he is a member of the national R&D team for thin-film photovoltaics in the US.

Nathan Lewis is George L. Argyros Professor of Chemistry at the California Institute of Technology, where he has been on the faculty since 1988. He has also served as the Principal Investigator of the Beckman Institute Molecular Materials Resource Center at Caltech since 1992. From 1981 to 1986, he was on the faculty at Stanford, as assistant professor from 1981 to 1985 and associate professor from 1986 to 1988. He received his PhD in Chemistry from the Massachusetts Institute of Technology. He has been an Alfred P. Sloan Fellow, a Camille and Henry Dreyfus Teacher-Scholar and a Presidential Young Investigator. He received the Fresenius Award in 1990, the ACS Award in Pure Chemistry in 1991, the Orton Memorial Lecture award in 2003

and the Princeton Environmental Award in 2003. He has published over 200 papers and supervised about 50 graduate students and postdoctoral associates. His research interests include light-induced electron transfer reactions, both at surfaces and in transition metal complexes, surface chemistry and photochemistry of semiconductor/liquid interfaces, novel uses of conducting organic polymers and polymer/conductor composites and development of sensor arrays that use pattern recognition algorithms to identify odorants, mimicking the mammalian olfaction process.

Tianquan Lian received his BS degree from Xiamen University in 1985, his MS degree from the Chinese Academy of Sciences in 1988 and his PhD from the University of Pennsylvania in 1993. After postdoctoral training in the University of California at Berkeley, he joined the faculty of chemistry department at Emory University in 1996. He was promoted to associate professor in 2002 and full professor in 2005. He has been a recipient of the NSF CAREER award and the Sloan fellowship. His research interest is focused on the ultrafast dynamics of nanomaterials and interfaces. He is particularly interested in fundamental physical chemistry problems related to nanomaterials-based solar energy conversion concepts and devices. These problems include the dynamics of electron transfer, energy transfer, vibrational energy relaxation and solvation at interfaces and in nanomaterials.

Stuart Licht has over 250 publications in renewable energy chemistry, physical chemistry and analytical chemistry, and was the recipient of the 2006 Electrochemical Energy Research Award. He has developed theory and experiment for the highly efficient solar generation of hydrogen fuel, introduced the contemporary use of caesium to enhance solar cell voltage and established the chemistry of an efficient solar cell that functions day and night. He has originated the field of Fe(VI) redox chemistry for charge storage (the ‘Super-Iron Battery’), as well as novel sulphur batteries and a variety of new aluminium electrochemical storage cells. En route to new pathways to utilise renewable energy, the Licht group continues to explore a range of fundamental physicochemical processes ranging from quantum mechanics to thermodynamics of water, hydrogen, halide, chalcogenide and transition metal chemistry, and to introduce new analytical methodologies, in dilute, concentrated or molten media, as needed to facilitate the research. Licht has chaired a regional section of the national American Chemical Society and also founded, and chaired, the New England, and the Israel, Sections of the Electrochemical Society.

Stephen Maldonado was a Beckman Scholar in 2000–2001 for his work on proton exchange membrane fuel cell system testing. After receiving a BS in Chemistry from the University of Iowa in 2001, he was awarded an NSF Fellowship and a Huntington Fellowship for graduate studies at the University of Texas at Austin. His thesis work centred on designing electrocatalytically active graphitic carbon nanotubes. In 2006, he obtained his PhD in Chemistry and joined the research laboratory of Professor Nathan S. Lewis as a postdoctoral research scientist at the California Institute of Technology. His current research focuses on the electrical and electrochemical properties of metal–silicon contacts using chemically modified silicon.

Rüdiger Memming obtained his PhD degree in Physical Chemistry from the University of Stuttgart, Germany, in 1958, working with Professor Förster, and then did post-doctoral work at the Chemistry Department of the University of Minnesota, Minneapolis, working with Professor R. S. Livingston for two years. In 1960, he started to work in the Philips Research Laboratory in Hamburg, Germany, where he continued until 1987. In addition, he had a research group at the Chemistry Department of the University of Hamburg from 1981 to 1987. After this he started a new government Institute for Solar Energy Research in Hanover, from which he retired in 1994. In 1991, he went to Japan for four months as a JSPS-Fellow.

R. J. Dwayne Miller obtained a BSc Honours degree in 1978 from the University of Manitoba and his PhD degree in Chemistry from Stanford University in 1983, and then did post-doctoral work as a NATO Science Fellow at the Université de Joseph Fourier, Grenoble. He started his academic research career at the University of Rochester in 1984, where he was a faculty member in Chemistry and the Institute of Optics. He relocated his research group to the University of Toronto in 1995, where he is currently the Director of the Institute for Optical Sciences and full professor in the Departments of Chemistry and Physics. He is a Fellow of the Royal Society of Canada and the holder of the Canada Research Chair in femtoscience. His early research interests focused on the primary events controlling electron transfer at surfaces. This work demonstrated how truly fast electron-transfer processes can be at conducting surfaces, and led to his current research, which focuses on femtosecond electron pulse generation to give atomic-level views of transition state processes. He welcomed the opportunity to return to his roots to write this review on the photophysical processes at semiconductor surfaces with the hope that this overview will help researchers solve the last hurdles to economically viable solar power.

Jenny Nelson is a Professor of Physics at Imperial College, London, where she has researched novel types of solar cell since 1989. Her current research focuses on photovoltaic energy conversion using molecular materials, characterisation of the charge transport, charge separation and morphological properties of molecular semiconductors, the theory of charge transport in organic semiconductors and modelling of photovoltaic device behaviour. She has published over 100 papers on photovoltaic materials and devices and a book on the physics of solar cells.

Arthur Nozik graduated from Cornell University in Chemical Engineering in 1959. After a brief spell in the aerospace industry, he entered Yale University to work for a PhD in physical chemistry. The birth of his daughter caused him to intermit these studies and join the American Cyanamid Company, but he returned to Yale and finished his PhD in 1967. He then returned to Cyanamid for seven years, introducing Mössbauer spectroscopy to the company. In 1974, he joined Allied Chemical Corporation to work on semiconductor photoelectrochemistry as applied to solar photoconversion. At Allied, he became the first to demonstrate the ‘zero bias’ photoelectrolysis of water, using an *n*-TiO₂ photoanode and a *p*-GaP photocathode, and also the photoreduction of dinitrogen on *p*-GaP. He also developed the ‘photochemical diode’, the forerunner of today’s particulate semiconductor suspensions. In 1978, he moved to the new Solar Energy Research Institute (now NREL) at Golden, Colorado, where he was Branch Chief of the Photoconversion Branch, 1980–1984, and has been a Senior Research Fellow since 1984. He was Team Leader of the NREL Chemical Sciences Team from 1985 to 2006 and he has been Professor Adjoint at the University of Colorado at Boulder since 1998. At NREL, his research has centred on the behaviour of hot carriers in quantum wells, superlattices and quantum dots. In 2005, thirty years of work in solar photon conversion were rewarded when he and his research group demonstrated efficient multiple exciton generation in lead chalcogenide quantum dots. He was awarded the 2008 Eni Award for Science and Technology.

Laurie Peter gained his PhD in Southampton in 1969, before being awarded a CIBA Postdoctoral Fellowship to work in the Group of Heinz Gerischer, who was then at the Technische Hochschule in Munich. Subsequently, he moved with Gerischer’s group to the Fritz Haber Institute in Berlin, where he remained as a member of staff until 1975, when he returned to the UK to take up a lectureship in Southampton. He remained in Southampton for the next 17 years and was promoted to professor before moving to Bath in 1992 to become Professor of Physical Chemistry and subsequently Head of Department. Laurie Peter was an editor of the *Journal of Electroanalytical*

Chemistry from 1999 to 2005, and has been awarded the Electrochemistry Prize of the Royal Society of Chemistry and the Pergamon Medal of the International Society of Electrochemistry. He currently leads the UK SUPERGEN Excitonic Solar Cell Consortium (Bath, Cambridge, Edinburgh and Imperial College), which is studying non-classical solar cells.

Nick Serpone obtained a BSc Honours Chemistry in 1964 from Sir George Williams University in Montreal and his PhD degree in Physical-Inorganic Chemistry from Cornell University in 1968, following which he joined the chemistry faculty of Concordia University as Assistant Professor. His early research involved NMR studies of Group IV coordination complexes. After sabbatical leaves at the University of Bologna, Italy, in 1975 and at the École Polytechnique Fédérale de Lausanne, Switzerland, as an invited professor in 1983, his research interests focused on the photochemistry of coordination complexes and on fundamental and applied studies in heterogeneous photocatalysis in which, together with others, he has been instrumental in developing the technology to degrade environmental organic pollutants and to dispose of toxic metals. In 1981, he co-founded the Canadian Centre for Picosecond Laser Spectroscopy at Concordia University and was its director until 2002. His other principal research interests have involved studies of ultra-fast photophysical and photochemical events in metal chalcogenide and silver halide semiconductors. Following his appointment as a University Research Professor and Professor Emeritus in 1998, he joined the Chemistry Division of the National Science Foundation in Washington DC as an IBO Program Director from 1998 to 2001. He was a Visiting Professor in Italy's programme 'Rientro dei Cervelli' at the University of Pavia from 2002 to 2005, where he carried out research into the photochemistry of sunscreen active agents.

Helmuth Tributsch obtained his PhD degree in physical chemistry at the Technical University, Munich, in 1968, working with Heinz Gerischer, and subsequently continued research with Melvin Calvin at the University of Berkeley. For the next ten years he worked in different institutions including Stanford University, the CNRS in Paris and the Fritz-Haber Institute in Berlin. Since 1982, he has been Professor of Physical Chemistry at the Free University in Berlin and head of the department at the Hahn-Meitner Institute specialising in research on sustainable energy systems.

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PREFACE

*Thus daily were my sympathies enlarged,
And thus the common range of visible things
Grew dear to me: already I began
To love the sun, a Boy I lov'd the sun,
Not as I since have lov'd him, as a pledge
And surety of our earthly life, a light
Which while we view we feel we are alive;
But, for this cause, that I had seen him lay
His beauty on the morning hills, had seen
The western mountain touch his setting orb,
In many a thoughtless hour, when, from excess
Of happiness, my blood appear'd to flow
With its own pleasure, and I breath'd with joy.*

William Wordsworth, *The Prelude: Book 2: School-Time*, 1805.

More solar energy falls on the Earth's surface every day than the total amount of energy the world's population would consume in 16 years at present rates of utilisation. To harness this potential to provide reliable and economic carbon-free sources of electricity and fuels remains a challenge, even in current times of high energy prices and action to mitigate climate change. However, there are encouraging signs. The annual global market for photovoltaic (PV) modules was valued at US\$12.9bn in 2007 and is predicted to grow by 15% compound per annum. Although crystalline silicon p - n junction cells still dominate this market, a new generation of photovoltaic and photoelectrochemical devices is emerging to challenge them, many based on the unique properties of matter at the nanoscale.

It is this new generation of solar photon conversion devices that are covered in this book. They are less highly developed than those described in Volumes 1 and 2 of this series, but their promise is at least as great. That promise is two-fold: on the one hand highly efficient devices with sophisticated architectures in which the Shockley–Queisser limit on efficiency is finally overcome, and on the other very low-cost plastic or organic-based devices that are cheap enough to be disposable.

The leitmotifs of these devices include bespoke dye sensitisers, space-quantised nanoscale structures that enable hot carrier or multiple exciton generation, molecular and solid-state junction architectures that lead to efficient exciton dissociation and charge separation, and charge collection by percolation through porous or mesoscale phases. Another common theme underlying the devices discussed in this book is the

orthogonalisation of the pathways for photon absorption and carrier collection. Contrast the classical silicon solar cell, in which the two pathways are parallel with an ETA or bulk heterojunction cell, in which they are orthogonal. In the silicon cell, the base layer has to be sufficiently thick to absorb incoming photons, so minority carrier diffusion lengths have to be (and are) as long as 200–500 μm , placing great demands on materials quality. In an ETA or bulk heterojunction cell, the junction architecture allows efficiencies of over 5% to be achieved with exciton or charge carrier diffusion lengths that are as much as one million times shorter, and materials of much lower electronic quality suffice.

Photocatalysis is closely related to photoelectrochemistry, and the fundamentals of both disciplines are covered in this volume. Their applications to photoelectrolysis and other solar fuel-forming or waste-destroying photochemical and photoelectrochemical processes will form the main subject matter of the fourth and final volume in this book series.

To satisfy the global need for carbon-free energy, the fields of photovoltaics and photoelectrochemistry must continue to develop. The key to progress lies in the quality of the fundamental research being conducted in this area. It is worrying that global funding streams for research to develop advanced solar photon conversion technologies remain fragile despite the concerted and powerful case for a ‘Manhattan project’ effort to do so made by the international scientific community during a special conference in 2005 on basic research needs for solar energy utilisation promoted by the US Department of Energy’s Office of Science, Basic Energy Sciences Division. However, commercialisation of some of these devices is beginning, and a January 2008 report from BCC Research predicts that the market for nanostructured thin films and silicon and dye-sensitised solar cells is set to grow at more than 50% per annum through to 2013 as the technology matures.

Our warmest appreciation goes to our fifteen authors, who between them have provided so rich a picture of the scientific frontiers they are exploring. We also thank Alexandra Anghel, Carol Burling, Barrie Clark and Stuart Honan for their editorial assistance, David Ginley, John Kelly and Reshef Tenne for providing information, James Bolton for his early input into some of the material in Chapters 1 and 4, the staff of World Scientific Press who expertly drew many of the diagrams, and Lenore Betts, Lizzie Bennett and Katie Lydon of IC Press for guiding us along the winding road to publication.

Mary D. Archer
Arthur J. Nozik

March 2008

CHAPTER 1

OVERVIEW

MARY D. ARCHER

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*Where from citadels on high
Her imperial standards fly,
Let the hot sun
Shine on, shine on.*

W. H. Auden, *Twelve Songs*, 1935–1938.

1.1 Themes

The major themes of this book are announced by its title: nanostructured and photoelectrochemical systems for solar energy conversion. It deals mainly with the direct, *i.e.* non-thermal, conversion of solar photonic energy into electrical power by photoelectrochemical or advanced photovoltaic means in extended-junction, mesoporous, nanocomposite or space-quantised structures and devices. Other themes are the fundamentals of electron transfer and photoinduced electron transfer in supramolecular assemblies, photocatalytic reactions at semiconductor dispersions, and experimental techniques for the characterisation of semiconductor photoelectrochemical systems.

Semiconductors have been the electrode materials of choice for solar photon conversion for nearly thirty years, on account of their favourable optoelectronic properties and chemical versatility. Semiconductor bandgap energies E_g commonly fall in the range 1–3 eV, which overlaps well with the spectrum of terrestrial sunlight, as shown in Fig. 9.1, and also with the decomposition potentials of such important reactions as water splitting, as shown in Fig. 2.17. Absorption by a semiconductor of photons of energy greater than the bandgap energy leads to the creation of ‘free’ holes and electron (in broadband inorganic semiconductors) and excitons (in organic semiconductors). At the junction of a photovoltaic device, these free carriers or excitons are separated into a flow of electrons in one direction and a flow of holes in the other at a potential difference determined by the light intensity and the junction characteristics, leading to the generation of electric power on illumination.

Photoelectrochemical cells for solar photon conversion are usually designed to produce either electric power or solar fuels; this book focuses on the latter. Power-producing solar cells are designed to be operated at their maximum-power point to produce electric power at the energy conversion efficiency η_{mp}

$$\eta_{\text{mp}} = \frac{i_{\text{mp}} V_{\text{mp}}}{E_{\text{o}}^{\text{s}}} \quad (1.1)$$

where E_{o}^{s} is the incident solar irradiance, i_{mp} is the maximum-power photocurrent density and V_{mp} is the maximum-power voltage. The ratio between the maximum power generated and the product of the short-circuit photocurrent density i_{sc} and the open-circuit voltage V_{oc} is known as the fill factor, η_{fill} . The higher the value of η_{fill} , the better the quality of the device.

$$\eta_{\text{fill}} = \frac{i_{\text{mp}} V_{\text{mp}}}{i_{\text{sc}} V_{\text{oc}}} \quad (1.2)$$

‘Classical’ silicon photovoltaic cells are capable of excellent performance, approaching the detailed balance limit for a single-bandgap device: non-concentrator single-crystal cells have reached an energy conversion efficiency¹ of 24.7%, and concentrator cells 27.6%. They are, however, minority-carrier devices, meaning that the photocurrent must be carried to the junction by electrons through *p*-type material, and by holes through *n*-type material. Minority carriers are highly susceptible to bulk recombination, as well as to trapping and interfacial recombination. A high level of materials quality and fastidious attention to cell design and fabrication are therefore needed to endow minority carriers in a silicon cell with sufficient lifetime to reach and flow across the junction without loss by hopping or recombination. The minimum thickness of a photovoltaic cell is determined by the width of the absorber layer needed to absorb incident light efficiently. Since crystalline silicon is an indirect-gap material, it is not intensely absorbing, and so a comparatively thick wafer of it is required to absorb incident sunlight efficiently, even with such refinements as surface texturisation, internal light scattering and back-surface reflection to increase the optical path length of light in the cell. Thus the excellent performance of the classical silicon photovoltaic cell is in some ways a triumph of materials and device optimisation over basically unfavourable materials characteristics. Few other inorganic semiconductors, and no organic semiconductors, are capable of being developed to deliver similarly good performance in a photovoltaic cell of classical, planar-junction architecture. Moreover, in a classical *p*–*n*

¹ Conversion efficiencies are, or should be, quoted for standard test conditions, which are 1000 W m⁻² of AM1.5 global insolation and a cell temperature of 25 C.

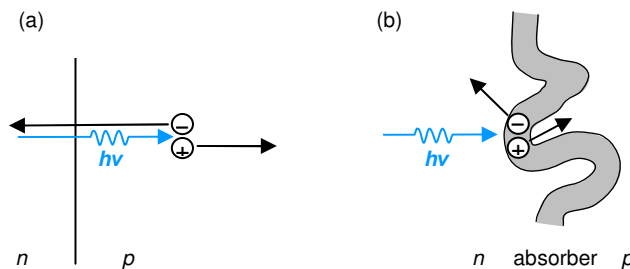


Figure 1.1 (a) Classical planar *n-on-p* photovoltaic cell junction, showing the dominant parallel direction of the light and charge separation pathways; (b) Extended, structured junction with interposed absorber layer (shaded in grey), showing the dominant non-parallel direction of the light and charge separation pathways.

junction cell the same material is required both to absorb light and to permit charge transport along the same dominant parallel pathway, which is perpendicular to the planar junction, as shown in Fig. 1.1a.

Extended-junction and nanostructured photoconversion devices can escape from these constraints by orthogonalising the pathways for light absorption and charge collection, as illustrated in Fig. 1.1b. The pathways for charge collection are much shorter, allowing the use of inexpensive low-quality materials, and also of organic semiconductors in which light absorption generates not free charge carriers but short-lived excitons that must reach an interface in order to separate at it and generate photocurrent. Additional and important advantages of nanosized semiconductor structures and particles are the increased carrier lifetimes arising from space quantisation, the enhanced redox potentials of photogenerated holes and electrons arising from the increased effective bandgap and the possibility of multiple exciton generation by one absorbed photon in a quantum dot.

In this chapter, I give an account of the historical development of semiconductor photoelectrochemistry and nanostructured photovoltaic devices in Section 1.2, and then Sections 1.3–1.6 provide a brief introduction to the major cell types discussed in the remainder of the book: the ETA (extremely thin absorber) cell, organic and hybrid cells, dye-sensitised solar cells (Grätzel cells) and regenerative solar cells.

In Chapter 2, Miller and Memming present an advanced treatment of the solid-state physics and photoelectrochemistry of semiconductors. In Chapter 3, my co-editor Art Nozik covers the fundamentals and applications of quantum-confined structures and explains how the unique ability of quantum dots to generate multiple pairs of charge carriers with a single high-energy photon could lead to a new generation of photovoltaic cells. In Chapter 4, I turn to electron-transfer theory, and how its understanding through

the powerful prism of Marcus theory has led to the design and synthesis of molecular dyads, triads and polyads with optimised hole–electron lifetimes and energies, which might in future be linked into energy-funnelling antennae or nanoscopic current-collecting systems to create molecular power-producing cells. Nick Serpone and Alexei Emeline provide a comprehensive account of the fundamentals of metal-oxide heterogeneous photocatalysis, with particular emphasis on dispersed titanium dioxide systems, in Chapter 5.

In Chapters 6–10, we turn to important cell types: inorganic extended-junction devices are described by Rolf Könenkamp, who has pioneered their development, in Chapter 6, and polymer and polymer-composite cells by Jenny Nelson and Jessica Benson-Smith in Chapter 7. In Chapter 8, dye-sensitised solar cells are discussed by James Durrant and their inventor, Michael Grätzel. Another authority in the field of solar photoelectrochemistry, Nate Lewis, and two colleagues, Stephen Maldonado and Anthony Fitch, provide an overview of non-dye-sensitised semiconductor/liquid junction solar cells in Chapter 9. In Chapter 10, Stuart Licht and Gary Hodes describe their own and others' development of photoelectrochemical storage (PECS) cells, which have the conceptual advantage over the other types of power-producing cell described in this volume of being able to produce continuous rather than intermittent power. Figure 1.2 shows how the performance of all these cell types has improved over time. Finally, Xin Ai and Tianquan Lian deal with the measurement of electron-transfer dynamics at the molecule/semiconductor interface in Chapter 11, and Laurie Peter and Helmut Tributsch cover techniques for the characterisation of photoelectrochemical systems in Chapter 12.

One type of photoelectrochemical device not covered in this book is the photogalvanic cell. By this term is meant power-producing or storage cells in which the products of an endoergonic photoredox reaction that occurs in solution are harvested at metal (or at any rate photoinactive) electrodes. Although Albery and Archer (1977) took a sanguine view of the maximum power conversion efficiency (5–9%) that might be obtained from such a cell, subsequent experimental studies have shown that the combination of long optical lengths, low diffusivities of short-lived redox products and imperfect electrode selectivity in practice restrict conversion efficiencies to well below 1%, rendering the photogalvanic cell impractical as a power-producing device (Archer and Ferreira, 1980).

Each chapter is comprehensively referenced, and the reader may also find some of the following recent reviews and books helpful: Fujishima and Zhang (2005), Soga (2006), Durrant *et al.* (2006), Hodes (2007), Kamat (2007) and Licht (2007). The Festschrift issue of the *Journal of Physical Chemistry* (Vol. 100, No. 50, 21 December 2006) in honour of my co-editor's seventieth birthday also contains many papers of relevance.

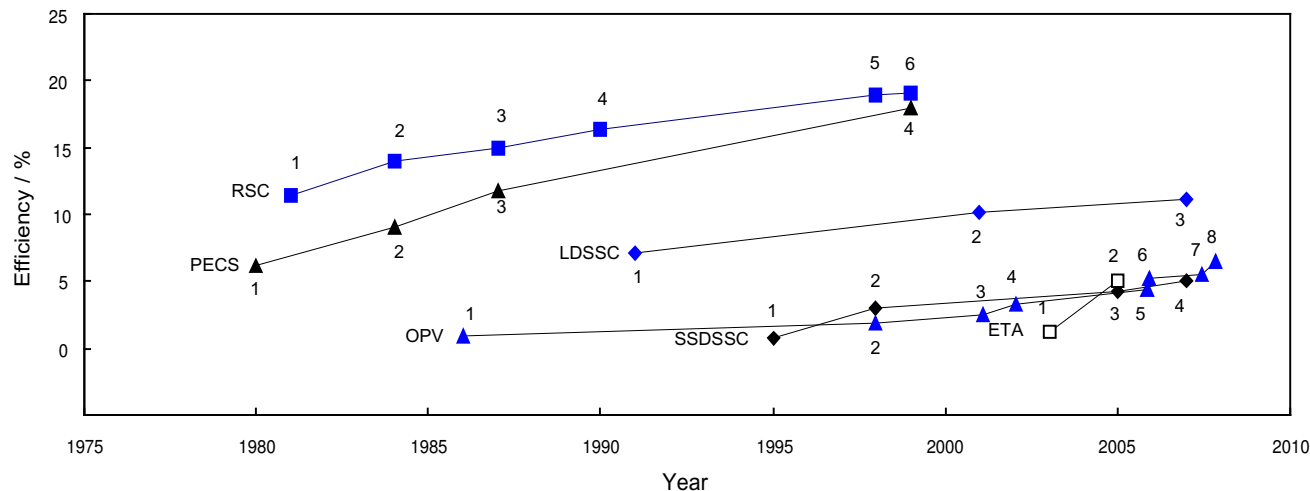


Figure 1.2 Best efficiencies by year of power-producing photoelectrochemical and nanostructured cells: ■ regenerative solar cells (RSC): 1 Heller (1981); 2 Gibbons *et al.* (1984); 3 Tufts *et al.* (1987); 4 Licht and Peramunage (1990); 5 Licht *et al.* (1998); 6 Licht *et al.* (1999); ▲ photoelectrochemical cells with storage (PECS): 1 Ang and Sammells (1980); 2 Keita and Nadjao (1984); 3 Licht *et al.* (1987); 4 Licht *et al.* (1999); ◆ liquid dye-sensitised solar cells (LDSSC): 1 O'Regan and Grätzel (1991); 2 Nazeeruddin *et al.* (2001); 3 Chiba *et al.* (2006); ◆ solid-state dye-sensitised solar cells (SSDSSC): 1 Tennakone *et al.* (1995); 2 Tennakone *et al.* (1998); 3 Schmidt-Mende *et al.* (2005); 4 Snaith *et al.* (2007); ▲ organic photovoltaic cells (OPV): 1 Tang (1986); 2 Granstrom *et al.* (1998); 3 Shaheen *et al.* (2001); 4 Brabec *et al.* (2002); 5 Li *et al.* (2005); 6 Reyes-Reyes *et al.* (2005); 7 Peet *et al.* (2007); 8 Kim *et al.* (2007); □ extremely thin absorber cells (ETA): 1 Ernst *et al.* (2003); 2 Nanu *et al.* (2005). All efficiency values are for standard or near-standard AM1.5G insolation; PECS4, RSC5, RSC6 and OPV8 are multijunction devices; all the others are single-junction devices.

1.2 Historical perspective

The first recorded observations of a photoelectrochemical (PEC) phenomenon were made by the young Henri Becquerel (Becquerel, 1839), who noted the photocurrent and photovoltage produced by sunlight acting on silver chloride-coated platinum electrodes in various electrolytes. Having satisfied himself that these effects were not thermal, Becquerel postulated that they resulted from a solid-state photochemical reaction, for which he obtained rough spectral response curves by the use of colour filters. Becquerel's interpretation of the photocurrent as a measure of 'le nombre de rayons chimiques' (the number of chemical rays) was vigorously challenged by the powerful Academician Jean Baptiste Biot (Biot, 1839), but over the next twenty years, Becquerel's view prevailed as he continued to work on silver halide-coated electrodes, developing a photoelectrochemical light meter based on AgCl (Becquerel, 1841–1867).

Pre-1940 PEC work on semiconducting films and electrodes was comprehensively reviewed by Copeland *et al.* (1941). Early work—mainly on the halides, oxides and sulphides of Ag, Cu and Hg in aqueous solution—was complicated by the photochemical instability of some of the materials used, notably the silver halides. Early workers generally interpreted the effects they saw in terms of photochemical reactions, particularly the pH-dependent photolysis of water, light-induced increases in solubility, activation of molecules by light and 'local cell' electrochemical activity, but gradually it was recognised that physical rectifying effects analogous to those in solid-state barrier cells were involved (*e.g.* Goldmann and Brodsky, 1914; Fink and Alpern, 1930; Müller and Spector, 1932; Roulleau, 1935, 1937).

Time-resolved studies of the photopotential of cyanine-sensitised AgBr revealed a biphasic response, ascribed by Sheppard *et al.* (1929, 1940) to the differing mobilities of electronic and ionic carriers. Work at Eastman Kodak by Leermakers *et al.* (1937) established the correspondence between the spectral photosensitisation of AgBr emulsions by cyanines and the absorption spectra of the dyes. The tendency for open-circuit photopotentials to increase with decreasing temperature was observed by Athanasiu (1925–1935), and the logarithmic dependence of photopotentials on irradiance by Sichling (1911). Several amperometric 'electrolytic photoelements' based on the photocurrent produced by the action of light on semiconductor electrodes, such as the Rayfoto and Arcturus Photolytic Cells ($\text{Cu/Cu}_2\text{O|Pb(NO}_3)_2(\text{aq})\text{|Pb}$ or Cu_2O), were commercialised in the 1930s (Fink and Alpern, 1930; Wilson, 1938; Lange, 1938; Fink and Adler, 1940).

During the forties and early fifties, Veselovskii (1941–1952) carried out extensive investigations on AgBr/Ag and oxidised Zn, Fe, Pb, Ag, Au and Pt, confirming by measurements of spectral sensitivity and quantum yield that the observed photo-

electrochemical effects were produced within a fairly thick oxide layer, and not by a surface reaction. Hillson and Rideal (1949) attempted to resolve the disputed mechanisms of hydrogen and oxygen evolution at various oxidised metal electrodes from photocurrent measurements. PEC effects were observed in Cu_2O (Kalita, 1935; Kasgkarev and Kosonogoya, 1948), oxidised Pb (Ginzburg and Veselovskii, 1952), Se (Pittman, 1953) and chlorophyll-sensitised ZnO, CdO and PbS (Putseiko, 1953).

Much pre-1955 work, carried out on semiconductors of uncontrolled properties and purity, was at best qualitative. Only after the crucial role of purity in controlling semiconductor properties had been recognised, and the nature of holes had been distinguished from that of positive ions, did systematic work on semiconductor electrodes become possible. The modern era of inorganic semiconductor electrochemistry began at Bell Telephone Laboratories with Brattain and Garrett's classical (1955) work on the current-voltage characteristics of *n*- and *p*-type Ge electrodes in aqueous solutions of KOH, KCl and HCl. This established that the current was controlled by the surface concentrations of holes and electrons, which were in turn controlled by the applied bias and could be increased by illumination. Dewald's (1959, 1960a) lucid expositions of the principles of semiconductor electrochemistry laid the foundation for rapid experimental advances in the sixties, when many important concepts were established: the relation between the sign of the photopotential and the conductivity type of the electrode (Williams, 1960); the concept of the flatband potential (Dewald, 1960b); valence-band and conduction-band electron-transfer kinetics (Gerischer, 1960, 1966); the mechanisms of photocorrosion (Williams, 1960; Turner, 1960) and suppression of semiconductor corrosion by common ions in solution (Barker, 1966); electrode surface states (Boddy and Brattain, 1962; Lazorenko-Manevich, 1962); work on *n*-Se and *p*-Se (Gobrecht *et al.*, 1959); KTaO_3 (Boddy *et al.*, 1968); oxygen evolution on illuminated anodically biased *n*- TiO_2 (Boddy, 1968) and SnO_2 (Möllers and Memming, 1972); and hydrogen evolution on illuminated cathodically biased *p*-GaP (Beckmann and Memming, 1969).

Despite these advances, semiconductor photoelectrochemistry remained the domain of a few specialists until the seminal announcement by Fujishima and Honda (1971, 1972) (prefigured in Fujishima *et al.*, 1969) of the sustained photoelectrolysis of water by the use of an *n*- TiO_2 photoanode, followed by the surge of interest in renewable energy produced by the 1973 oil price shock. Fujishima and Honda's 1972 *Nature* paper, although reporting no hitherto unknown phenomena, reoriented research towards the glittering prize of solar photoelectrochemical water splitting and power production using inexpensive polycrystalline semiconductor electrodes. Since then, the pursuit of this and related goals has transformed semiconductor photoelectrochemistry from a specialist domain into a major interdisciplinary subject.

The use of nanoscale constructs has given a further major boost to solar photon conversion. The scale of nanosized materials such as quantum dots and nanotubes, conventionally taken to lie in the range 1–100 nm, produces very interesting size quantisation effects in optoelectronic and other properties: bandgaps shift to the blue, carrier lifetimes increase, potent catalytic properties emerge and constructs with very high surface-to-volume ratios can be made. Incorporation of nanoscale structures in photovoltaic devices allows these unique properties to be exploited, with conversion efficiencies above the detailed balance limit becoming possible in principle.

Nanosized TiO_2 powders are of outstanding importance in this context. Aqueous suspensions of ~ 30 nm particulate TiO_2 (mostly in the rutile form) are the active agent in many of the photocatalytic systems described by Serpone and Emeline in Chapter 5. Agglomerations of TiO_2 nanoparticles into mesoporous films of pore size 2–50 nm which allow the penetration of liquid are the basis of the important dye-sensitised solar cell (DSSC) discussed by Grätzel and Durrant in Chapter 8, as well as most of the hybrid devices described by Nelson and Benson-Smith in Chapter 7, and some of the ETA (Extremely Thin Absorber) cells described by Könenkamp in Chapter 6. The term ‘eta-solar cell’ was actually introduced by Könenkamp and co-workers (Siebentritt *et al.*, 1997), who had earlier used the term ‘sensitisation cell’ for the same type of device (Wahi and Könenkamp, 1992). Precursors to ETA cells with liquid electrolytes as hole conductors were developed by Vogel *et al.* (1990), Ennaoui *et al.* (1992) and Weller (1993). Similar electrolytic cells with RuS_2 (Ashokkumar *et al.*, 1994) and InP (Zaban *et al.*, 1998) nanoparticle absorbers have also been demonstrated.

Size quantisation effects in the photoelectrochemistry of semiconductors were first demonstrated by Nozik *et al.* (1985) in a strained-layer superlattice electrode with 40 alternating layers of undoped GaAs and $\text{GaAs}_{0.5}\text{P}_{0.50}$ (in which charge carriers were spatially confined in one dimension in the GaAs quantum wells). Quantum dots (in which charge carriers are spatially confined in three dimensions) were first used in photoelectrochemistry by Kietzmann *et al.* (1991) to sensitise TiO_2 in Grätzel-type cells, and in a photovoltaic device by Greenham *et al.* (1996), who observed quantum efficiencies of up to 12% in conjugated polymer/CdX (X = Se or S) nanocrystal composite solar cells. Multiple exciton generation in quantum dots was first observed by Schaller and Klimov (2004) in PbSe QDs, and efforts to incorporate quantum-dot arrays into next-generation solar cells are now underway (Service, 2008).

The history of organic semiconductors goes back further, although only in recent years have organic solar cells revealed their full potential. The first observation of high conductivity in an organic polymer was made by Bolto *et al.* (1963) in polypyrrole that had been partially oxidised by iodine doping. Semiconducting device (FET) properties were first noted in organic materials by Heilmeyer *et al.* (1964) in copper phthalocyanine,

and later by McGinness *et al.* (1974) in melanin, a naturally derived material which is a complex copolymer of polyacetylene, polypyrrole and polyaniline. In a later paper, Shirakawa *et al.* (1977) reported high conductivity in partially oxidised polyacetylene, work for which he and his colleagues Alan MacDiarmid and Alan Heeger won the 2000 Nobel Prize in Chemistry.

These discoveries have created a new industry based on organic semiconductors, one spin-off from which has been the development of organic solar cells. These function rather differently from 'classical' inorganic cells. Photon absorption in an organic semiconductor generates, not 'free' charge carriers as in a broad-band inorganic semiconductor, but excitons which do not spontaneously separate but will dissociate at a heterojunction yielding separate charges, provided the interface presents a sufficient electrochemical potential drop. The first 'modern' organic solar cell was the planar bilayer device of Tang (1986), but this cell architecture is limited because the exciton must be generated within a few diffusion lengths of the heterojunction to have a reasonable chance of being collected. Exciton diffusion lengths are typically <10 nm, and this limits the thickness, and hence the absorbance, of a planar bilayer cell. The highly folded architecture of the dispersed or bulk heterojunction (BHJ) cell, which came onto the scene in the 1990s, overcomes this problem. Halls *et al.* (1995) published one of the first studies showing that a dispersed heterojunction, formed from a phase-separated blend of donor-type and acceptor-type polymers in which the domain size is of the order of an exciton diffusion length, greatly improved the quantum efficiency of exciton dissociation and charge generation. Yu *et al.* (1995) reported a quantum efficiency of 29% and an energy conversion efficiency of about 2.9% for a BHJ cell containing a blend of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH-PPV) with C₆₀. Yoshino *et al.* (1997) introduced a three-layer structure into a polymer donor-acceptor blend cell, which improved performance further. Hummelen *et al.* (1995) developed solubilised fullerenes such as [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM; Fig. 7.1 shows its structure), thus enabling the casting of well-blended bulk heterojunctions of two phases from a single solvent.

Further breakthroughs in organic solar cell performance came in 2000–2001. Stephen Forrest and co-workers achieved 2.4% efficiency in a Tang-like copper phthalocyanine/ perylene tetracarboxylic derivative cell by incorporating an exciton-blocking layer between the photoactive organic layers and the metal cathode to prevent exciton quenching at the cathode (Peumans *et al.*, 2000). The Linz and Groningen groups improved the efficiency of the conjugated polymer/methanofullerene cell to 2.5% by using a more intimate blend of the two phases (Shaheen *et al.*, 2001). At the same time, Michael Grätzel improved the performance of the all-solid-state dye-sensitised solar cell

to 2.56% by blending the hole conductor *spiro*-OMeTAD with 4-*tert*-butylpyridine and $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ to control junction recombination (Krüger *et al.*, 2001).

In the next four sections of this chapter, we shall look at the operating principles of those cells that are the subject of specialist chapters later in the book. All are designed to produce electric power. Most have highly extended interfaces (as illustrated in Fig. 1.1) to increase light absorption and/or charge separation. Given the steady improvements in efficiency shown in Fig. 1.2, there is a good prospect of further efficiency gains and wider commercial application of one or more of these newer cell types.

1.3 Extremely thin absorber (ETA) cells

ETA (Extremely Thin Absorber) cells are the subject of Chapter 6 by Könenkamp, and here we provide only a brief introduction and overview. An ETA cell is an inorganic all-solid-state photovoltaic cell with a structured electron-conducting substrate, usually an *n*-type semiconducting oxide such as TiO_2 or ZnO , and a solid hole-conducting superstrate, usually a *p*-type semiconductor such as CuSCN , CuAlO_2 , PEDOT or *spiro*-OMeTAD. In between the two is sandwiched an extremely thin (~ 5 – 150 nm) layer of a strongly absorbing inorganic semiconductor such as a-Si:H (Wahi and Könenkamp, 1992), CdTe or CdS (Siebentritt *et al.*, 1997) or CuInS_2 (Möller *et al.*, 1998). The absorber can be in the form of either a continuous layer or nanoparticles of a semiconductor such as PbS (Wienke *et al.*, 2003). In some devices, the hole conductor is omitted and the absorber is contacted directly by a metal contact.

Figure 1.3 shows the two most common ETA cell structures, in which the substrate morphology is either mesoporous (Fig. 1.3a) or columnar (Fig. 1.3b). As in the dye-sensitised cells discussed in Section 1.5, the extended interface interposes many individual absorber layers in the path of incoming light, allowing good total light absorption although each individual absorber layer is very thin. The interfacial morphology should be rough on the wavelength scale of sunlight (~ 500 nm), so that the incoming light beam is strongly scattered, thus increasing the optical path length of light within the cell. Light is further trapped by internal reflection in the absorber layers. The holes and electrons that are generated by light absorption within the absorber layer have only a very short distance to travel to the interface with the electron and hole conductor, respectively, allowing efficient carrier collection from absorber materials with poor transport properties. Hence low-cost materials and inexpensive fabrication processes can be used to make ETA cells. As Könenkamp explains in Chapter 6, the main difficulty in fabricating ETA cells is achieving conformal, void-filling deposition of the absorber on the substrate, and then of the hole conductor (if present) on the absorber.

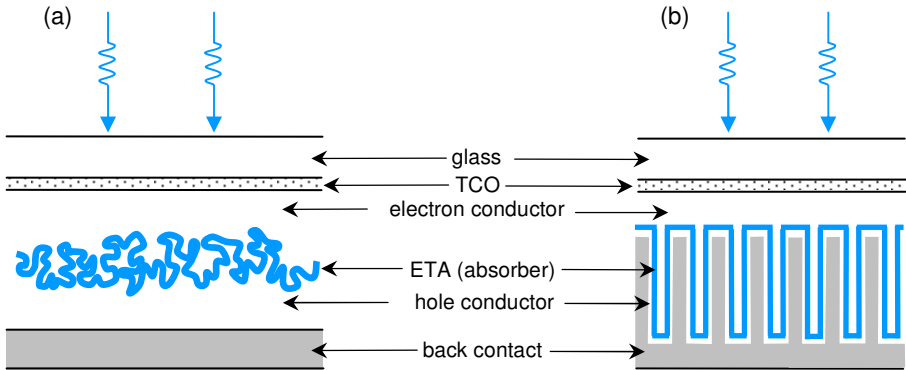


Figure 1.3 Typical ETA cell geometries. The interfaces between the absorber and electron and hole transport layers are structured, usually in porous (Fig. 1.3a) or columnar (Fig. 1.3b) form. The interfaces between the transport layers and the contact layers are planar. If the substrate morphology is porous, both transport layers should be transparent to avoid shadowing effects. The contact layer on the light entry side must be transparent and the back contact should be reflective, to minimise optical losses outside the absorber layer. If the interfacial structuring is not very deep, it is possible to omit the hole transport layer, and deposit the back contact straight onto the ETA layer, which greatly simplifies device fabrication.

Figure 1.4 shows the band structure of a typical ETA cell. Electronically speaking, these are *p-i-n* junction cells, the light absorber being the *i*-layer and the built-in field persisting throughout the thin transport layers under most bias conditions. Incoming light generates hole–electron pairs in the absorber, which separate into free carriers, as is normal in inorganic semiconductors. The field in the absorber layer assists carrier transport and hence very short carrier diffusion lengths (as low as ~ 10 nm) can be tolerated. The photogenerated electrons are injected into the conduction band of the electron conductor, and the holes into the valence band of the hole conductor. These separated charges then travel across the transport layers to the contacts under majority-carrier transport conditions without the risk of recombination. However, the extended junction, despite its optical advantages, may also be responsible for the dominant loss mechanism in most ETA cells, namely interface recombination at defect and boundary sites of the large solid/solid interface areas.

At their present state of development, ETA cells typically exhibit open-circuit voltages of 0.6–0.7 V and photocurrents of $5\text{--}15\text{ mA cm}^{-2}$. While the fill factors in the earlier ETA cells were often poor, typically $\sim 20\%$, more recent cells have improved fill factors, typically $\sim 60\%$. Overall, the solar conversion efficiencies are modest, as shown in Fig. 1.2; to date η_{mp} values of approximately 5% have been obtained (Nanu *et al.*, 2005). Insertion of an ultrathin tunnel barrier layer of an insulator such as Al_2O_3 or MgO can improve the open-circuit voltage (Wienke *et al.*, 2003). Incorporation of quantum

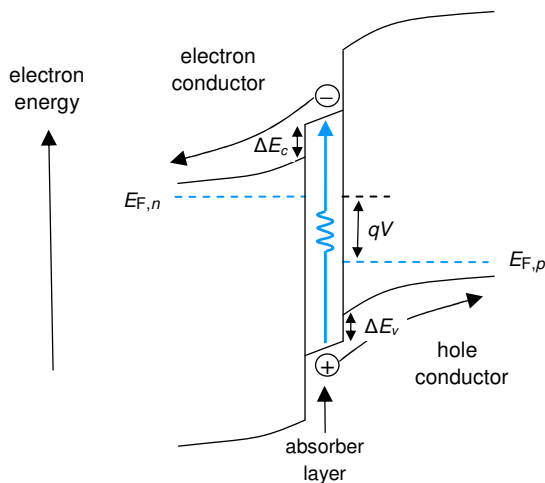


Figure 1.4 Band structure in an ETA cell, showing the majority-carrier quasi-Fermi levels $E_{F,n}$ and $E_{F,p}$ in the electron and hole conductor, respectively, and the photovoltage V . The conduction-band edge of the absorber must be above that of the electron conductor, while the valence-band edge of the absorber must be below that of the hole conductor. The conduction-band and valence-band offsets ΔE_c and ΔE_v between the electron or hole conductor and the absorber should be sufficient to suppress back electron or hole transfer, but not so great as to cause a substantial loss of photovoltage; ΔE_c and ΔE_v values of ~ 0.2 – 0.3 V are optimal.

dots within the absorber layer may enhance carrier lifetimes, as well as introducing the possibility of a two-state excitation process (Luque and Marti, 1997) or multiple exciton generation (as discussed in Chapter 3).

The technology of ETA cells is not yet mature, and future improvements in their efficiency can reasonably be expected. Modelling calculations (Taretto and Rau, 2005) indicate that 15% efficient CdTe ETA cells are possible even at electron diffusion lengths as low as 10 nm, provided that the built-in voltage is optimised to restrict recombination over the working bias range of the cell. If efficiency improvements of this order can be achieved and fabrication methods can be satisfactorily scaled up, ETA cells could offer a low-cost, stable alternative to traditional photovoltaic cells and dye-sensitised solar cells.

1.4 Organic solar cells

Organic solar cells are photovoltaic devices containing thin (typically ~ 100 nm) films of light-absorbing organic semiconductors such as conjugated polymers or small molecules. The term ‘organic solar cell’ is something of a misnomer, since some of the most efficient devices contain (essentially inorganic) fullerene derivatives as electron

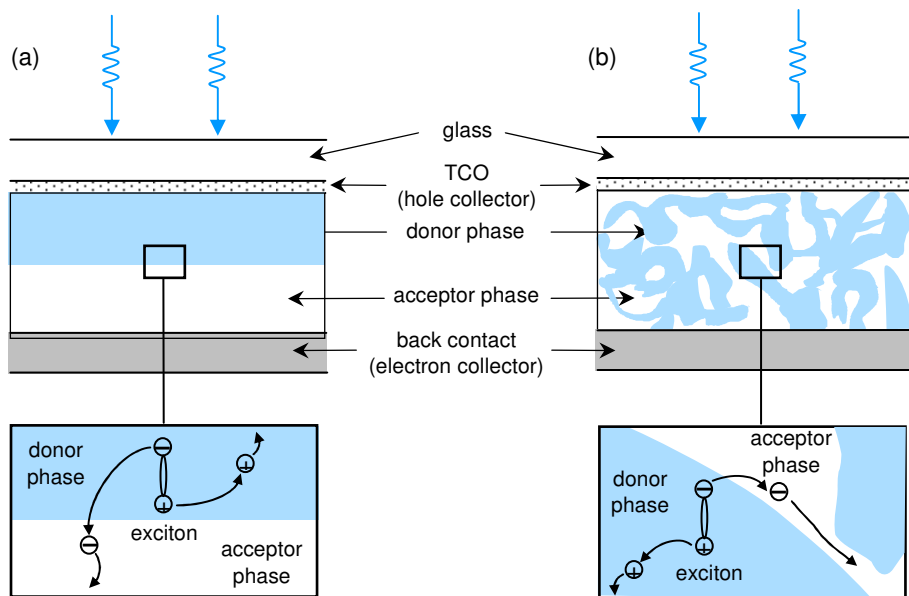


Figure 1.5 Typical organic photovoltaic cell architectures. (a) Bilayer cell; (b) bulk heterojunction cell.

acceptors. Nevertheless, the term ‘organic solar cell’ and its equivalent, ‘organic photovoltaics’ (OPV), are a convenient shorthand which we, like others, shall use for both purely organic and hybrid organic/inorganic devices.

Jessica-Benson Smith and Jenny Nelson cover OPV in detail in Chapter 7, and here again we provide only a brief introduction. Polymer-based solar cells have been recently reviewed by Mayer *et al.* (2007). Figure 1.5 shows two typical cell architectures for OPV (Fig. 7.4 shows two more). The first (Fig. 1.5a) is a simple bilayer device in which an electron-donating layer and an electron-accepting layer of two different organic semiconductors form a planar junction at which light-generated excitons dissociate into charge carriers and are collected at the electrodes. The bilayer copper phthalocyanine/perylene tetracarboxylic derivative (CuPc/PTC) cell developed by Tang (1986) was the pioneer in this field, with a power conversion efficiency of 0.95%. Currently the best-performing bilayer cells have efficiencies of around 5% (see Fig. 1.2), and contain a vacuum-deposited molecular layer of a metal phthalocyanine as the light absorber and electron donor and a fullerene derivative as electron acceptor.

The other common OPV cell type, shown in Fig. 1.5b, is the bulk heterojunction (BHJ) cell, sometimes called the dispersed heterojunction cell. These cells contain intimate three-dimensional blends of the electron-donating and electron-accepting

materials, which creates a very large-area interface between the two phases. Provided the phase domain size is of the order of twice the exciton diffusion length, the probability of exciton capture and dissociation is much increased. The blend may be random, as in Fig. 1.5b, or it may be vertically graduated or ordered as in the right-hand diagram of Fig. 1.3. Currently the most efficient BHJ cells are made by co-deposition from solution of a solubilised electron-donating polythiophene polymer together with a solubilised electron-accepting fullerene derivative. At the time of writing, the world record efficiency of 5.5% for a single-junction organic solar cell is held by the polymer/fullerene derivative cell made by Alan Heeger's group (Peet *et al.*, 2007), in which a few volume per cent of alkanedithiols is incorporated to improve the bulk heterojunction morphology. The related tandem (double-junction) BHJ cell developed by Heeger's group (Kim *et al.*, 2007), which has a front cell of a low-bandgap polymer/fullerene composite connected by a transparent TiO_2 layer to a back cell of a lower-bandgap polymer/fullerene composite, has a reported efficiency of 6.5% for light intensity of 200 mW cm^{-2} . Ordered heterojunctions have not so far yielded such good performance: the best ordered nanostructured oxide/polymer hybrid device is only 0.4% efficient.

The photovoltaic effect in organic solar cells arises, not from formation of free charge carriers in one or both phases, as in a classical silicon p - n junction cell, but from exciton dissociation at the junction between the two phases. Photon absorption in organic semiconductors, whether small molecules or polymers, does not generate free holes and

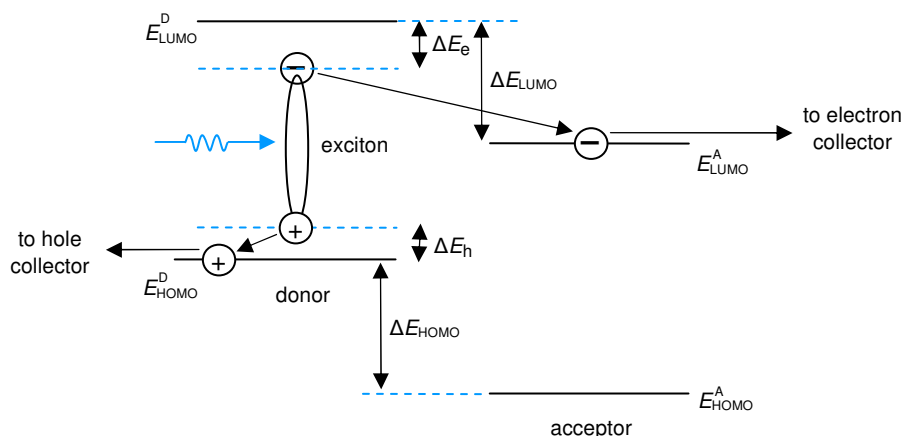


Figure 1.6 Exciton formation and charge separation in a bulk heterojunction, for the case that the donor phase absorbs the incident light. The energies of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of the donor (D) and acceptor (A) phases are shown. The exciton binding energy ΔE_{b} is $(\Delta E_{\text{e}} + \Delta E_{\text{h}})$.

electrons, but rather hole–electron pairs known as excitons, normally in the singlet state. These are bound together by Coulomb attraction and in some cases by local lattice relaxation, with typical binding energies of ~ 0.5 eV. Such excitons are short-lived and have low mobility, with typical diffusion lengths of <10 nm before they recombine. However, if such excitons are formed sufficiently close to an interface with appropriate band offsets, they will reach it by diffusion and dissociate into separate charges, as shown in Fig. 1.6 for the case that light is absorbed in the donor phase. The exciton, which has binding energy $\Delta E_b = \Delta E_c + \Delta E_h$, will dissociate at the heterojunction, injecting an electron into the acceptor phase, provided that $\Delta E_{\text{LUMO}} > \Delta E_b$, where ΔE_{LUMO} is the LUMO band offset between the two phases. Similarly, an exciton formed in the acceptor phase will dissociate spontaneously at the heterojunction provided that $\Delta E_{\text{HOMO}} > \Delta E_b$, where ΔE_{HOMO} is the HOMO band offset. In either case, electrons then diffuse through the acceptor phase to the electron-collecting electrode, and holes through the donor phase to the hole-collecting electrode. The diffusion pathway is straightforward in the bilayer cell, but requires the donor and acceptor phases to form continuous interpenetrating networks in the BHJ.

The moving charge usually takes the form of a polaron, which is a charge surrounded by a locally polarised lattice. Polarisation slows the moving charges; fullerene derivatives probably owe their superior performance to the high electron affinity and small lattice distortion (and consequent relatively high mobility) of the fullerene radical anion $\text{C}_{60}^{\bullet-}$. Polymer donor phases usually form hole polarons that are delocalised over a segment of the polymer backbone, and hence are also relatively mobile.

The electron-collecting electrode should form an ohmic contact to the acceptor LUMO and hence have a relatively low work function, while the hole-collecting electrode should have a relatively high work function. Apart from this, the performance of a bilayer cell is not very sensitive to the nature of the electrodes, since field-assisted migration is not a significant mode of carrier transport. The performance of a randomly-blended BHJ cell, on the other hand, is critically dependent on the electrodes being sufficiently different to form a conducting (ohmic) contact to the ‘right’ phase and a blocking contact to the ‘wrong’ phase. If this is not the case, the internal hole and electron photocurrents in a random BHJ will be shorted at the electrode(s). An alternative stratagem is to grade the vertical composition of the cell from a 0:100 blend of the two components at one electrode to 100:0 at the other.

Organic solar cells show considerable promise. They have the advantages over inorganic solar cells of being mechanically flexible, lightweight, and disposable with little environmental impact. The constituents can be made soluble so they can be made by low-cost, low-temperature solution-processing methods that should be easily scalable up. The rapid advance in the technology of OLEDs (organic light-emitting diodes) is helping

in that it is fertilising research on organic polymer cells, for example through the synthesis of organic semiconductors with improved properties and electrodes with the right electronic properties for selective electron transfer. However, OPV have some way to go before they can become a commercial reality. Their efficiency must be improved by extending the absorption edge towards the red or beyond, reducing the energy loss in the charge-separation step by better band-edge alignment, improving charge-carrier mobilities and (in the BHJ) reducing the dead ends and isolated domains that trap charge carriers. Device stability also requires attention.

1.5 Dye-sensitised solar cells (Grätzel cells)

The architecture of the original dye-sensitised solar cell (DSSC) reported by O'Regan and Grätzel (1991) is shown in Fig. 1.7a (see also Fig. 8.1). This consisted of two conducting glass electrodes, one coated with a compact but highly porous film of TiO_2 on which was adsorbed a ruthenium polypyridyl dye, and the other platinised, separated by a solution containing a high concentration of the iodide/triiodide redox couple in an organic solvent. These mesoscopic solar cells—to give them the name preferred by their inventors—or Grätzel cells—to give them the name quickly conferred on them by others—had a reported efficiency of 7.1% in simulated sunlight. This provoked some raised eyebrows, because the cell architecture broke many of the existing 'rules' about how to make an efficient cell—the dye layer was only a monolayer thick, so each layer absorbed only very little light, the interface was hugely extended, leading to abundant opportunities for back reaction, and the nanocrystalline TiO_2 semiconductor was full of electron traps. However, fifteen years later, the mode of action of the cell is well understood, laboratory DSSCs have reached over 11% efficiency, and commercial cells are becoming available for portable power applications.

Grätzel and Durrant discuss the DSSC fully in Chapter 8, and Mori and Yanigada (2006) have provided a recent review. In brief, these cells owe their good performance to a happy combination of factors. The TiO_2 layer in the DSSC is about $10\text{ }\mu\text{m}$ thick and has a roughness factor of over 1000, providing a very large surface area for dye adsorption. Incident light is efficiently scattered into the TiO_2 layer and absorbed by the many successive dye monolayers through which the light passes. The photoactive state of the Ru dye (a long-lived triplet) injects an electron into the TiO_2 conduction band in an ultrafast and efficient process, shown in Fig. 1.7b and in more detail in Fig. 8.4, creating an open-circuit photopotential of $\sim 0.8\text{V}$ under standard operating conditions. The cell is a majority-carrier device, so the injected electrons can diffuse through the TiO_2 to the collecting anode with no danger from bulk recombination—there is little or no interfacial

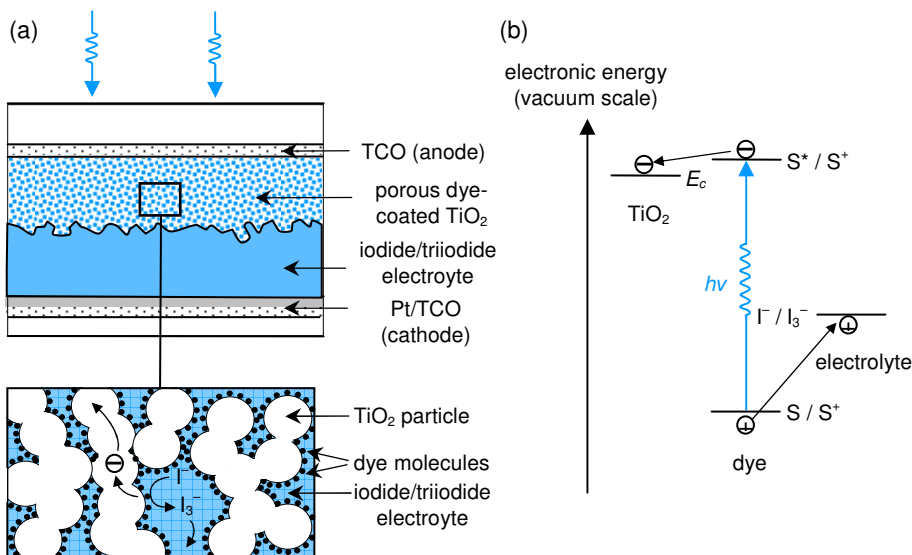


Figure 1.7 Dye-sensitized solar cell (a) cell architecture; (b) electronic energy levels. The placement of the semiconductor band-edge energy E_c and the solution Fermi levels S/S^+ , S^*/S^+ and I^-/I_3^- on the same scale, the vacuum scale of electronic energy, is explained in Appendix 1A at the end of this chapter.

electric field because of the screening effect of ions in the solution in the electrode pores—and the quantum efficiency of charge collection can approach unity in optimal conditions. The oxidised dye is quickly restored to its ground state by electron transfer from iodide, and the electric circuit is completed by the reduction of iodine, mainly complexed as triiodide, to iodide at the counter electrode. Crucially, the unwanted interfacial charge-recombination reaction



is slow compared with electron transport across the TiO₂ layer primarily because it is a two-step process involving high-energy I⁻-like intermediates. This reaction is, however, fast at the counter electrode—as it needs to be to avoid significant overpotential loss—because platinum catalyses the reaction by adsorption of the intermediates. In some views, the dye layer also contributes to the slowness of the back reaction at the photoelectrode by physically blocking access of triiodide to the TiO₂.

The various loss mechanisms in the DSSC, and what is being done to reduce their impact, are discussed in Chapter 8. The first is poor light absorption near the band edge of the dyes commonly used in the cell, which limits device short-circuit current; the

second is further minimisation of interfacial recombination losses, which, whilst already being relative minor at short circuit, accelerate as the device operation moves towards open circuit and are the primary limitation of device voltage output. In practical terms, the ‘classical’ Grätzel cell also suffers from the corrosive nature of iodine and the possibility of leakage of the liquid electrolyte. The use of gel electrolytes and ionic liquids has gone some way to solving these problems. More radically, the ionic electrolyte has been replaced by electronic hole conductors in a later generation of all-solid-state cells that have now reached efficiencies of over 5% (see Fig. 1.2), and the semiconductor (TiO_2 or ZnO) has been engineered into nanorods to shorten the pathway for electron collection (Baxter and Aydil, 2006; Pan *et al.*, 2007).

In commercial terms, the main advantage that DSSCs have over silicon *p-n* junction cells is that their cost per watt could be four to five times lower, because of their lower-cost materials and construction techniques. Moreover, the efficiency of DSSCs falls off less in low-intensity light or with increasing temperature than that of Si cells, and they have lower embodied energy (*i.e.* less energy is required to make them). DSSCs can also be fabricated as translucent panels or laid down as flexible films on non-planar surfaces.

There is considerable commercial interest in DSSCs. They could make striking additions to buildings as power-generating coloured ‘glass’ panels, and a demonstration of a building-integrated application by the Japanese company Aisin Seiki is described in Chapter 8. In autumn 2006, Konarka Technologies Inc. (Lowell, Mass., USA), which has produced some cells for testing by the US military, joined with the Ecole Polytechnique Fédérale de Lausanne, where Michael Grätzel and co-workers developed the original DSSC, to license a 30-MW European facility for the production of flexible, foil-backed DSSCs to G24 Innovations Ltd. (www.g24i.com), a new company based in Cardiff, Wales, which has recently started to ship mobile phone charger units. Also in autumn 2006, the Australian company Dyesol (www.dyesol.com) acquired the Lausanne-based Greatcell Solar SA and is working towards the industrialization of DSSC. The Rhode Island-based Solaris Nanosciences Corporation (www.solarisnano.com) has demonstrated *in-situ* replacement of degraded dye in the DSSC, and Hydrogen Solar (www.hydrogensolar.com), a private company based in Surrey, UK, has developed a ‘Tandem Cell’ in which a DSSC is combined with an Fe_2O_3 -based photoelectrolysis to achieve water splitting.

1.6 Regenerative solar cells

Regenerative solar cells (RSCs), also known as semiconductor/liquid photoelectrochemical cells, electrochemical photovoltaic solar cells, wet photovoltaic cells or liquid-

junction solar cells, are single-compartment electrochemical batteries that produce electrical power on illumination without any net chemical change occurring in the cell. They normally comprise one semiconductor photoelectrode, which may be *n*- or *p*-type, an electrolyte phase containing a redox couple O,R, and a non-light-sensitive counter electrode that is reversible to the same redox couple. The source of the cell emf is the photopotential of the illuminated semiconductor electrode. Illumination of this electrode drives the redox reaction $O + e^- \rightleftharpoons R$ in the non-spontaneous direction at an electrode potential at which it cannot occur in the dark. The reaction is reversed at the counter electrode. The cell therefore produces electric power without net chemical change, unlike a conventional battery in which the reagents are depleted as current is drawn.

It is possible to construct a regenerative cell with two photoelectrodes and a suitable redox couple, and hence to increase the output voltage. The photoelectrode of an RSC may be dye-sensitised; the Grätzel cell discussed in the preceding section and in Chapter 8 is the prime example of such a cell. However, the principles of RSC operation are essentially the same whether the photoelectrode is sensitised or not.

In a practical device, the cell geometry must allow for the illumination of the semiconductor/solution interface, and the ohmic resistance of the cell should be minimised to avoid internal power loss. This is best achieved in a thin-layer device in which the semiconductor electrode faces the Sun and is illuminated through the electrolyte and the counter electrode. The counter electrode should therefore either be translucent or coarsely gridded.

A number of RSCs of good efficiency were developed in the late 1970s and the 1980s. In Chapter 9, Nate Lewis and his fellow researchers discuss the types of photoelectrode used in RSCs—mainly crystalline or amorphous silicon, III–V semiconductors, cadmium chalcogenides or lamellar or ternary chalcogenides—and the stratagems that have been adopted to stabilise their performance; these include judicious choice of the redox couple and solvent to avoid corrosion, chemical modification or metallisation of the photoelectrode surface and passivation of surface traps and defects. Table 9.1, at the end of Chapter 9, gives an extensive compendium of RSC characteristics and performance; Table 1.1 shows selected cells of high efficiency from this table.

Figure 1.8 shows cell schematics for two generic non-dye-sensitised regenerative solar cells (RSCs) based on either an *n*-type or a *p*-type semiconductor electrode. Figure 1.8a shows the cell $n\text{-SC} | \text{O,R} | \text{CE}$, in which the electrode *n*-SC is an *n*-type semiconductor photoanode, CE is the counter electrode and O,R is the redox couple. R is oxidised to O at the illuminated *n*-SC, while O is reduced to R at CE. Figure 1.8b shows the analogous RSC based on the *p*-type semiconductor photocathode *p*-SC. In both cases, the photoelectrode operates in the potential range between its flatband potential U_{fb} and the standard potential $U_{O,R}^0$ of the redox couple, as shown in the bottom diagram.

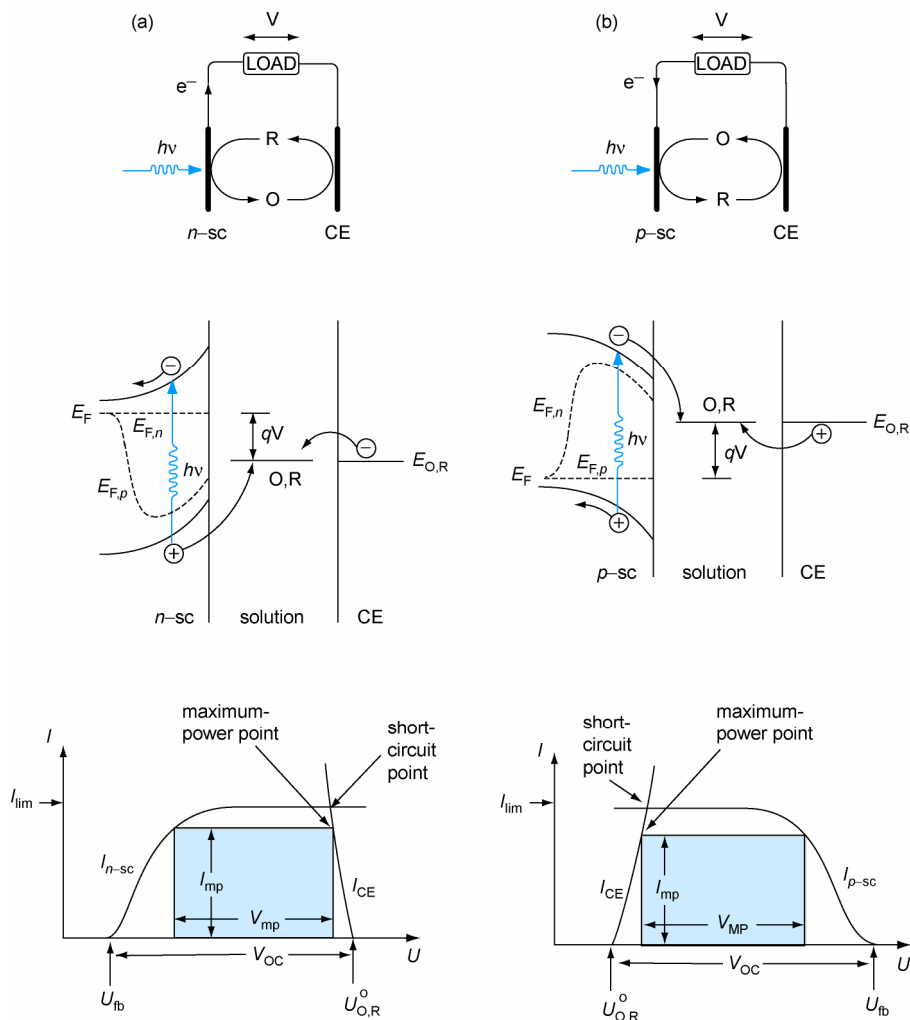


Figure 1.8 Cell schematics for a regenerative solar cell based on (a) an *n*-type photoelectrode; (b) a *p*-type photoelectrode. The top diagrams show the cell reactions under illumination, the middle diagrams the electronic energy levels and band bending, and the bottom diagrams the cell current-voltage ($I-U$) characteristics with the photoelectrode and counter electrode (CE) currents shown in the same quadrant. The maximum power point is located at the point on the current-voltage curve at which the rectangle of maximum area may be inscribed in this quadrant. The photovoltage V , the electron and hole quasi-Fermi levels $E_{F,n}$ and $E_{F,p}$ and the solution Fermi level $E_{O,R}$, the open-circuit potential U_{OC} of the photoelectrode and the standard redox potential $U_{O,R}^0$ of the O,R redox couple are also shown.

Table 1.1 Maximum-power conversion efficiency of selected regenerative solar cells

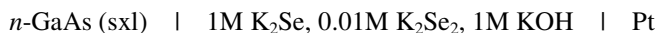
Cell ^a	$\eta_{\text{mp}}/\%$	Reference ^b
$n\text{-Si} \mid \text{Me}_2\text{Fc}^+, \text{Me}_2\text{Fc}, 1\text{M LiClO}_4 \text{ in } \text{CH}_3\text{OH} \mid \text{CE}$	14	Gibbons <i>et al.</i> (1984)
$p\text{-InP} \mid \text{V}^{3+}, \text{V}^{2+}, 4\text{M HCl} \mid \text{CE}$	11.5	Heller (1981)
$n\text{-GaAs} (\text{Os}^{3+}) \mid \text{Se}_n^{2-}, \text{Se}^{2-}, 1\text{M KOH} \mid \text{CE}$	15	Tufts <i>et al.</i> (1987)
$n\text{-CdSe}_{0.65}\text{Te}_{0.35} \mid 3\text{M S}_2, 1.8\text{M KOH} \mid \text{CE}$	12	Licht <i>et al.</i> (1985)
$n\text{-MoSe}_2 \mid \text{I}_3^-, 2\text{M KI} \mid \text{CE}$	9	Kline <i>et al.</i> (1981)
$n\text{-CuInSe}_2 \mid \text{I}_3^-, \text{I}^-, 0.1\text{M Cu}^{2+}, 0.01\text{M In}^{3+}, 6\text{M KI} \mid \text{CE}$	12	Menezes <i>et al.</i> (1984)

^a CE = counter electrode. The solvent is water in all cases except for the first-listed cell.

^b Full citations are given at the end of Chapter 9.

The cell delivers current I at voltage V . Neglecting the effect of internal resistance, qV is the difference between the quasi-Fermi level E_{F} of the illuminated photoelectrode and the Fermi level $E_{\text{O,R}}$ of the redox solution.² The counter electrode should be virtually non-polarised so its potential departs little from $U_{\text{O,R}}^0$ when current is drawn. The two electrodes need not have the same area but must pass the same current.

The photocurrent delivered by the photoelectrode should rise steeply from the open-circuit potential and reach its limiting value I_{lim} before the maximum-power point, so that the cell has a good fill factor with the short-circuit current $I_{\text{sc}} \approx I_{\text{lim}}$. This requires a semiconductor electrode of good optoelectronic properties, so that the rise of the photocurrent from the flatband potential is not slowed by such factors as hole–electron recombination. The photopotential delivered by the photoelectrode should not be limited by Fermi-level pinning. O,R should be present in high concentration to avoid concentration polarisation at either electrode. A high concentration of background electrolyte is usually required to provide adequate solution conductivity. Miller and Memming discuss the factors governing the performance of RSCs in more detail in Section 2.5.1 of Chapter 2. The cell of Tufts *et al.* (1987)



in which the photoelectrode was an Os^{3+} -treated (100) oriented matte-etched $10\text{ }\mu\text{m}$ thick $n\text{-GaAs}$ epitaxially-grown layer on a conducting $n^+\text{-GaAs}$ substrate and protected from photoanodic corrosion by the $\text{Se}_2^{2-}, \text{Se}^{2-}$ redox couple, is an example of a highly efficient single-junction cell ($V_{\text{oc}} = 0.78\text{--}0.81\text{ V}$, $i_{\text{sc}} = 24\text{--}26\text{ mA cm}^{-2}$, $\eta_{\text{fill}} = 0.65\text{--}0.75$, $\eta_{\text{mp}} = 15.0 \pm 1.0\%$). It is possible to increase RSC performance further by use of a multijunction photoelectrode, which is in effect a semiconductor photoelectrode in series with one or

² The concept of the solution Fermi level is discussed in Appendix 1A at the end of this chapter.

more buried photovoltaic junctions. For example, the RSC of Licht *et al.* (1998) with its GaAs/Si dual-bandgap photoelectrode had a reported solar-to-electric power conversion efficiency of 19–20%. (Figure 10.14 shows the same photoelectrode deployed in a photoelectrochemical storage cell.)

Figure 1.9 shows cell schematics for an RSC with two photoelectrodes. The photovoltage is increased but, as the bottom diagram shows, the current output is limited by the photoelectrode that delivers the smaller limiting current, in this example the p -type

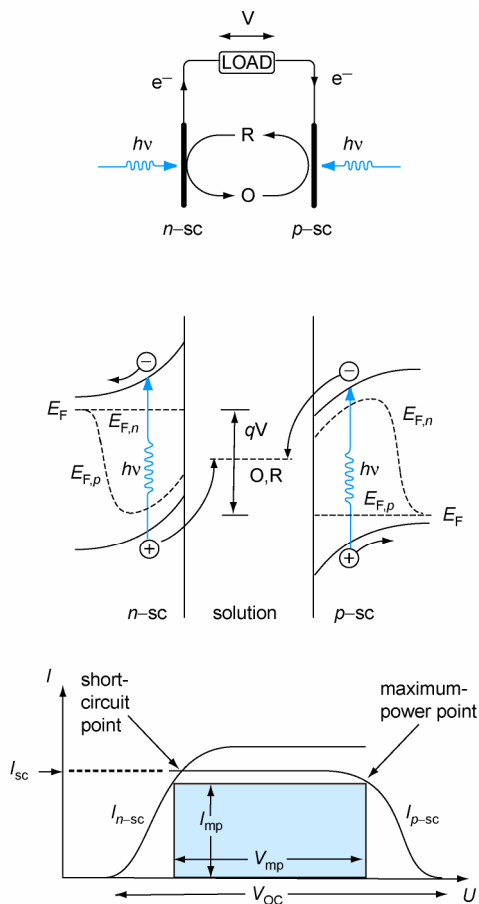


Figure 1.9 Cell schematics for a regenerative solar cell with both an n -type photoelectrode and a p -type photoelectrode. The top diagram shows the cell reaction under illumination, the middle diagram the electronic energy levels and band bending, and the bottom diagram the cell current–voltage (I – U) characteristic with both anode and cathode currents shown in the same quadrant. The maximum condition is shown by the rectangle. Other symbols as shown for Fig. 1.8.

electrode. For optimal performance, the limiting currents of the two photoelectrodes need to be the same. Such cells have generally been constructed to increase the voltage in a water-splitting cell to allow the unassisted photoelectrolysis of water: The $n\text{-TiO}_2/p\text{-GaP}$ water-splitting cell of Nozik (1976) is a good example. Fornarini *et al.* (1984) investigated the energetics of a number of p/n cells for photoelectrolysis that could also be used in regenerative mode.

As Table 9.1 shows, the efficiencies of non-dye sensitised RSCs can match all but the best single-junction solid-state photovoltaic cells. However, for practical applications short-term efficiency is not the main criterion of merit—cost and long-term operational stability are more important.

1.7 Future prospects

Some of the cells discussed in this book are being commercially developed, some are currently the subjects of intense research activity, while others have been of less interest or even dormant in recent years. The latter are included for completeness and also because—you never know. Already the novel properties of nanostructured materials and ongoing advances in the performance of organic semiconductors are prompting a re-evaluation of some older photoconversion devices, previously discarded on the grounds of inefficiency or instability. At the same time, combinatorial methods in synthesis allow large numbers of novel materials to be examined. In molecules, optical transitions can be tuned synthetically through molecular design. In semiconductors, optoelectronic properties are transformed by size quantisation; crystalline silicon, for example, which is an indirect-gap material in the bulk, becomes increasingly direct-gap-like in small nanocrystals (Kovalev *et al.*, 1998). Hole–electron lifetimes are greatly extended: both upconversion and down-conversion (multiple exciton generation) become possible. Structural perfection is achievable in size-quantised structures because defects cannot be energetically tolerated. New opportunities in surface protection and junction stabilisation are opened by the application of caps to nanostructures. Formed shapes such as nanorods and nanocones allow better pathways for charge-carrier transport to be engineered. Multijunction architectures are a promising route to improving cell efficiencies, and various configurations are possible (Licht, 1998 and 2001), although matching the currents while ensuring that photons are not wasted and that each sub-cell operates near its maximum-power point is challenging.

All in all, we can predict—or even allow ourselves to imagine—further exciting advances in the science and technology of solar photon conversion in nanostructured and photoelectrochemical systems in the years ahead.

APPENDIX 1A

THE VACUUM SCALE OF ELECTRODE POTENTIAL AND THE CONCEPT OF THE SOLUTION FERMİ LEVEL

It is often helpful in photoelectrochemistry to locate electronic energy levels in the electrode and solution on a common scale. This appendix explains how this can be achieved by defining the so-called vacuum scale of electrode potential, which is referenced to the energy of an electron in a vacuum.

The simplest cell that could be used to measure an electrode potential would contain two electrodes, two leads and three interfaces



where *sl* and *el* are the solution and electrode in the half-cell whose potential is to be measured, *M* is a reference electrode which is made of a metal that also constitutes the lead, and the metal *M'* of the other lead is identical to *M* except for its electrostatic inner potential ϕ . Figure 1A.1 shows the potential differences across the various interfaces of this cell.

The cell emf U_{cell} is the difference in inner potential between the two chemically identical leads, which we can write in the following ways

$$U_{\text{cell}} = \phi^{M'} - \phi^M \quad (1A.1)$$

$$= (\phi^{M'} - \phi^{el}) + (\phi^{el} - \phi^{sl}) - (\phi^M - \phi^{sl}) \quad (1A.2)$$

$$= \Delta_{el}^{M'}\phi + \Delta_{sl}^{el}\phi - \Delta_{sl}^M\phi \quad (1A.3)$$

where $\Delta_{\beta}^{\alpha}\phi$ denotes the difference in inner potential between phases α and β . We would like to split U_{cell} into two electrode potentials

$$U_{\text{cell}} = U_{el/sl} - U_{\text{ref}} \quad (1A.4)$$

but it is clear from eq. 1A.3 that this separation is not straightforward because there are (at least) three interfaces³ across which there are potential differences in the cell. For example, the choice of $\Delta_{sl}^{el}\phi$ for $U_{el/sl}$ would be unsuitable, first because it is not measurable and second, because it leaves the first term in eq. 1A.3 unaccounted for.

³ The argument that follows would be unaffected if the cell contained additional interfaces: these would introduce more terms in eq. 1A.2 *et seq.*, but these would cancel out.

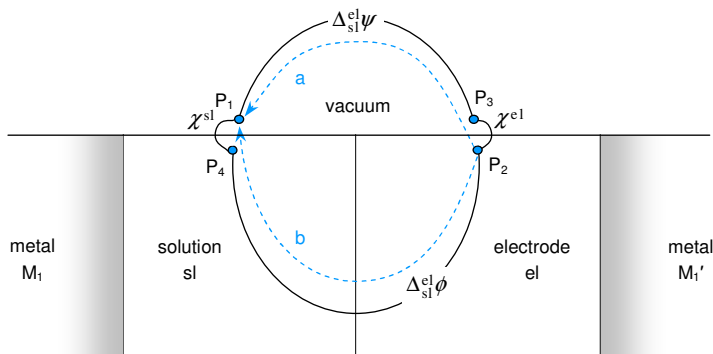
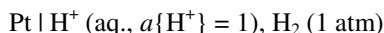


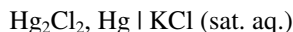
Figure 1A.1 Inner (ϕ), outer (ψ) and contact (χ) potential differences for the cell $M | sl | el | M'$. P_1 is a point just outside the solution phase (sl); P_2 is just inside the electrode phase (el).

1A.1 SHE and SCE scales of electrode potential

The standard hydrogen electrode (SHE) scale of electrode potential proposed by Nernst (1900) circumvents this difficulty and remains in widespread use. On this scale, zero is defined by setting $U_{SHE}^o = 0$ for the standard hydrogen electrode



at all temperatures. Thus the electrode potential of any electrode system *vs.* SHE is the emf of a cell consisting of that system as one half-cell and the SHE as the other. Since the SHE is not easy to set up or use, the more convenient saturated calomel electrode (SCE)



for which $U_{SCE} = 0.2444 - 0.0025(T - 298) \text{ V vs. SHE}$, is often used as a subsidiary reference electrode.

1A.2 Absolute electrode potentials

The SHE and SCE scales do not allow electrode potentials to be directly compared with the electronic energy levels (such as the band-edge energies of a semiconductor) in the electrode. To do this, we need a scale of electrode potential based, not on a reference electrode, but on a reference electronic energy level. A good choice, which allows different electrodes to be compared in the same solvent, is the *local vacuum level* of the

solution. This is the energy of an electron at point P₁ in Fig. 1A.1, which is just outside the solution phase. The *absolute electrode potential* $U_{\text{el/sl}}$ (abs) of the sl/el half-cell may then be defined by reference to the work required to remove an electron from the interior of the electrode to the local vacuum above the solution (Frumkin and Damaskin, 1975, 1977; Gerischer and Ekardt, 1983; Trasatti, 1986a). This can be expressed in terms of measurable quantities by dividing the terms in eq. 1A.2 in a different way. The electrode el is in electronic equilibrium with the metal lead M' so the electrochemical potential⁴ of an electron in the two phases must be the same, *i.e.* $\tilde{\mu}_{\text{e}}^{\text{el}} = \tilde{\mu}_{\text{e}}^{\text{M'}}$. Moreover, metals M and M' are chemically identical so the chemical potential of an electron is the same in the two phases, *i.e.* $\mu_{\text{e}}^{\text{M}} = \mu_{\text{e}}^{\text{M'}}$. Therefore

$$\phi^{\text{M'}} - \phi^{\text{el}} = \Delta_{\text{el}}^{\text{M'}} \phi = \frac{1}{q}(\mu_{\text{e}}^{\text{M'}} - \mu_{\text{e}}^{\text{el}}) = \frac{1}{q}(\mu_{\text{e}}^{\text{M}} - \mu_{\text{e}}^{\text{el}}) \quad (1A.5)$$

Substitution of eq. 1A.5 into eq. 1A.3 gives the cell emf as

$$U_{\text{cell}} = \left[\Delta_{\text{sl}}^{\text{el}} \phi - \frac{\mu_{\text{e}}^{\text{el}}}{q} \right] - \left[\Delta_{\text{sl}}^{\text{M}} \phi - \frac{\mu_{\text{e}}^{\text{M}}}{q} \right] \quad (1A.6)$$

The two bracketed expressions in eq. 1A.6 do not contain quantities relating to other interfaces and are termed *single electrode potentials*. We can turn them into absolute potentials expressed with respect to the local solution vacuum level by adding to each the surface potential⁵ χ^{sl} of the solution, which is the electric potential difference between a point just inside the solution phase and just outside it (points P₄ and P₁ in Fig. 1A.1)

$$U_{\text{cell}} = \left[\Delta_{\text{sl}}^{\text{el}} \phi - \frac{\mu_{\text{e}}^{\text{el}}}{q} + \chi^{\text{sl}} \right] - \left[\Delta_{\text{sl}}^{\text{M}} \phi - \frac{\mu_{\text{e}}^{\text{M}}}{q} + \chi^{\text{sl}} \right] \quad (1A.7)$$

and noting from Fig. 1A.1 that

$$\Delta_{\text{sl}}^{\text{el}} \phi = \Delta_{\text{P}_4}^{\text{P}_2} \phi = \Delta_{\text{P}_3}^{\text{P}_2} \phi + \Delta_{\text{P}_1}^{\text{P}_3} \phi + \Delta_{\text{P}_4}^{\text{P}_1} \phi = \chi^{\text{el}} + \Delta_{\text{sl}}^{\text{el}} \psi - \chi^{\text{sl}} \quad (1A.8)$$

⁴ The *electrochemical potential* $\tilde{\mu}_i^\alpha$ (Guggenheim, 1929) of a charged particle *i* in phase *α* is the work that must be done in reversible isothermal transfer of one particle (one mole of particles in some texts) from a field-free vacuum to the interior of the phase. It is the sum of a chemical and an electrical component: $\tilde{\mu}_i^\alpha = \mu_i^\alpha + z_i q \phi^\alpha$, where μ_i^α is the chemical potential of *i* in phase *α* and z_i is the algebraic number of electronic charges *q* on *i*. For an electron, $z_i = -1$.

⁵ Surface potentials arise from electronic polarisation and (in a polar solvent) dipole orientation of the solvent molecules at the free surface of the solution.

where $\Delta_{\text{sl}}^{\text{el}}\psi$ is the outer or contact potential difference between the electrode and solution phases; contact potential differences are measurable quantities.

Substituting from eq. 1A.8 for χ^{sl} in the first bracketed term of eq. 1A.7, we obtain

$$U_{\text{cell}} = \left[\Delta_{\text{sl}}^{\text{el}}\psi - \frac{\mu_{\text{e}}^{\text{el}}}{q} + \chi^{\text{el}} \right] - \left[\Delta_{\text{sl}}^{\text{M}}\phi - \frac{\mu_{\text{e}}^{\text{M}}}{q} + \chi^{\text{sl}} \right] \quad (1A.9)$$

where the two bracketed terms are now the *absolute electrode potentials* of the two electrodes. We may relate the first of these terms to the work function Φ^{el} of the electrode, which is the minimum work required to remove an electron from the interior of the uncharged phase el (for which $\psi = 0$) to a field-free vacuum, by noting that this is the same quantity, but with the opposite sign, as the electrochemical potential of an electron in the uncharged phase, *i.e.*

$$\Phi^{\text{el}} = -\mu_{\text{e}}^{\text{el}} + q\chi^{\text{el}} \quad (1A.10)$$

Noting that the first bracketed term of eq. 1A.9 is the absolute potential $U_{\text{el/sl}}(\text{abs})$ of the sl/el half-cell, and using eq. 1A.10, we can now write

$$U_{\text{el/sl}}(\text{abs}) = \Delta_{\text{sl}}^{\text{el}}\psi - \frac{\mu_{\text{e}}^{\text{el}}}{q} + \chi^{\text{el}} \quad (1A.11)$$

$$= \Delta_{\text{sl}}^{\text{el}}\psi + \frac{\Phi^{\text{el}}}{q} \quad (1A.12)$$

Equations 1A.11 and 1A.12 correspond to paths *a* and *b* respectively between points P_2 and P_1 in Fig. 1A.1. Thus $qU_{\text{el/sl}}(\text{abs})$ is the energy of an electron at the local vacuum level of the solution (point P_1) compared with that of an electron at the Fermi level in the electrode (point P_2). Both terms on the right-hand side of eq. 1A.12 are measurable, so in principle $U_{\text{el/sl}}(\text{abs})$ is also measurable.

1A.3 Absolute electrode potential of the SHE

To create a scale of electrode potentials based on eq. 1A.12, we need to know the contact potential difference between the solution phase of a suitable reference electrode system and the electrode itself. The most accurate measurements of this type have been made by using the standard hydrogen electrode as the reference electrode and mercury, the work function of which is known to good accuracy (although it is not normally used in the SHE), as the reference metal. Equation 1A.12 then gives

$$U_{\text{SHE}}^{\circ}(\text{abs}) = \Delta_{\text{sl}}^{\text{Hg}} \psi^{\circ} + \frac{\Phi^{\text{Hg}}}{q} \quad (1\text{A.13})$$

where $\Delta_{\text{sl}}^{\text{Hg}} \psi^{\circ}$ is the contact potential difference between mercury and the SHE solution under standard conditions. Contact potential measurements by McTigue and co-workers (Farrell and McTigue, 1982, 1984; Borazio *et al.*, 1985) have refined Randles' (1956) work and yield the value (Parsons, 1985; Trasatti, 1986a, 1986b)

$$U_{\text{SHE}}^{\circ}(\text{abs}) = 4.44 \pm 0.02 \text{ V at } 298.15 \text{ K} \quad (1\text{A.14})$$

The 20 mV error derives from the uncertainty in the work function of mercury. Equation 1A.14 indicates that the work required to transfer an electron from the interior of the equilibrated SHE electrode to a point just outside the solution phase is $4.44 \pm 0.02 \text{ eV}$.

1A.4 The solution Fermi level

The concept of the 'solution Fermi level' is very useful in photoelectrochemistry, although it strikes some as strange at first, because the term 'Fermi level' was first introduced and defined for an electronically conducting phase, such as a metal or semiconductor, which contains 'free' electrons.⁶ In this context, the Fermi level E_{F} is defined as the energy, measured with respect any convenient reference level, for which the probability that an electronic energy level is occupied is one-half. The most convenient reference level to use in photoelectrochemistry is the local vacuum level of the solution. The Fermi level of any conducting phase α is then synonymous with the electrochemical potential of an electron in that phase, *i.e.* $E_{\text{F}}^{\alpha} = \tilde{\mu}_{\text{e}}^{\alpha}$.

The solution phase of an electrochemical cell does not contain 'free' electrons, but it does generally contain a redox couple which can equilibrate with the 'free' electrons in the electrode. This allows us to extend the concept of the Fermi level to the solution. Consider the redox couple O,R in contact with an electrode el at which the redox reaction $\text{O} + n\text{e}^{-} \rightleftharpoons \text{R}$ occurs. When the system is at equilibrium, the work of transferring an electron across the electrode/solution interface to transform $(1/n)\text{O}$ to $(1/n)\text{R}$ is zero, *i.e.*

$$\tilde{\mu}_{\text{O}}^{\text{sl}} + n\tilde{\mu}_{\text{e}}^{\text{el}}(\text{equilibrium}) = \tilde{\mu}_{\text{R}}^{\text{sl}} \quad (1\text{A.15})$$

⁶ Moreover, the use of the term 'Fermi level' for non-fermionic solution species has been criticised by Reiss (1985); but see also Pleskov and Gurevich (1986), pp. 58–59.

Now $\tilde{\mu}_e^{\text{el}}$ (equilibrium) is the Fermi level E_F^{el} of any electrode that is in equilibrium with the O,R redox couple. This also defines the Fermi level of the redox couple in solution, to which we shall give the symbol $E_{\text{O,R}}$.

$$E_F^{\text{el}}(\text{equilibrium}) = \tilde{\mu}_e^{\text{el}}(\text{equilibrium}) = \frac{1}{n}(\tilde{\mu}_R^{\text{sl}} - \tilde{\mu}_O^{\text{sl}}) = E_{\text{O,R}} \quad (1\text{A.16})$$

Figure 1A.2 shows this equivalence, together with typical density-of-states functions for the energy levels in a semiconductor electrode and a solution containing a redox couple. As this figure illustrates, the Fermi level does not necessarily correspond to an actual electronic energy level in the phase.

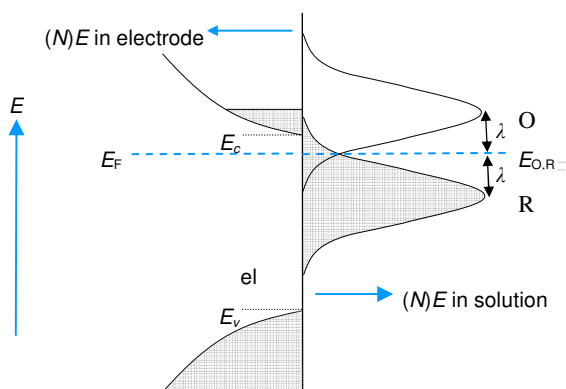


Figure 1A.2 Diagram to show the equivalence of the Fermi level E_F of an electrode, shown here as an *n*-type semiconductor, with the solution Fermi level $E_{\text{O,R}}$ of a redox couple O,R in equilibrium with the electrode. The diagram also shows typical occupied (shaded) and unoccupied (unshaded) density-of-states distributions $N(E)$ in each phase. In the electrode, the density-of-states functions curve parabolically from the band-edge energies U_c and U_v . In the solution, the occupied (R) levels and unoccupied (O) levels are broadened by the fluctuating solvent environment to Gaussian distributions, the maxima of which are offset from each other by 2λ , where λ is the Marcus reorganisation energy.

1A.5 Vacuum scale of electrode potential

We are now in a position to relate the electronic energy levels of the solution and the electrode on the same scale. It follows from the definition of absolute electrode potential and its value for the SHE, given in eq. 1A.14, that the solution Fermi level $E_{\text{O,R}}$ of a redox couple O,R is related to its electrode potential $U_{\text{O,R}}$ (SHE) on the SHE scale by

$$E_{\text{O,R}} = -qU_{\text{O,R}}(\text{abs}) = -qU_{\text{O,R}}(\text{SHE}) - 4.44 \pm 0.02 \quad (1\text{A.17})$$

Figure 1A.3 illustrates this important relation between the two scales. The positive direction on the SHE scale corresponds to increasingly positive inner potential of the electrode, and hence to decreasing energy of electrons in the electrode.

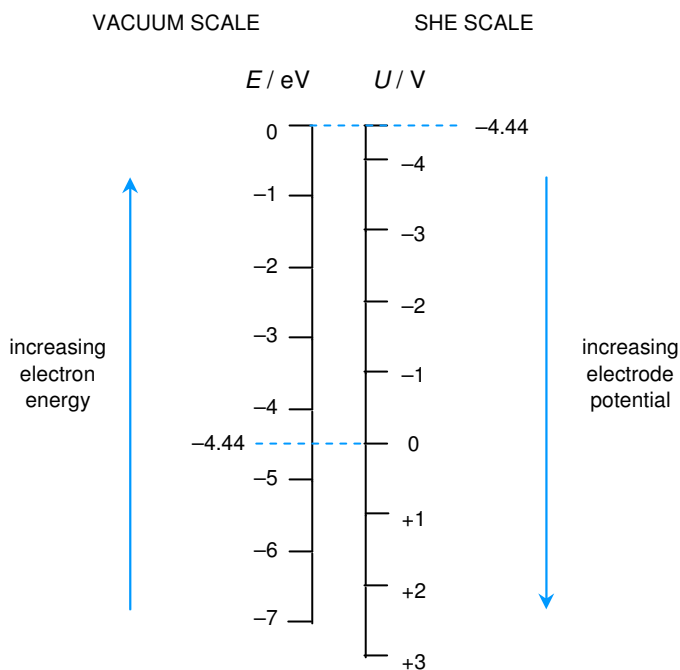


Figure 1A.3 Relation between the vacuum scale of electron energy E and the standard hydrogen electrode (SHE) scale of electrode potential U .

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CHAPTER 2

FUNDAMENTALS IN PHOTOELECTROCHEMISTRY¹

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*As far as we can discern, the sole purpose of human existence is
to kindle a light of meaning in the darkness of mere being*

Carl Jung, *Memories, Dreams, Reflections*, 1962

2.1 Introduction

The earliest photoelectrochemical experiment was reported by Becquerel in 1839 when he found a photovoltaic effect at an illuminated silver chloride electrode. The full understanding of this phenomenon was not achieved until 1954, when Brattain and Garrett showed how electrochemical reactions occurring at Ge electrodes could be influenced by changing the semiconductor properties of germanium, and also by light excitation. This early work was rapidly followed up between 1954 and 1970 by investigation of several other semiconductor electrodes. These studies established the first models for the nature of charge distribution, and the kinetics and energetics of charge transfer across the semiconductor–liquid interface. All these studies in semiconductor electrochemistry prior to 1970 were of a purely fundamental nature.

¹ The authors submitted the final version of this manuscript in 2001. Owing to subsequent delays in the preparation of this book series, most of the references in this chapter date from then. This chapter provides the fundamental basis of photoelectrochemistry in terms of the underlying photophysics and photochemistry and as such it forms an important starting point in the treatment of solar energy conversion. The editors have updated references where appropriate.

In the early seventies, the potential application of photoelectrochemical systems to solar energy conversion and storage was recognised. Photoelectrochemical systems are in principle applicable for solar energy conversion into electrical energy, as well as for the production of a chemical fuel. The photoelectrolysis of H_2O using sunlight is especially attractive because hydrogen is a valuable energy carrier and is more easily stored than electricity. During photoelectrolysis, radiant energy is converted into chemical free energy in the form of high-energy chemical products—that is, the chemical free energy change in the liquid is positive. Where chemical reactions in the liquid have a negative free energy change, the process is termed photocatalysis. In this case, the reaction runs downhill in energy. An important application of such reactions is the photocatalytic mineralisation of organic waste. The simple construction of electrode–electrolyte interfaces makes these systems highly attractive alternatives to more costly all-solid-state solar conversion devices. Moreover, photoelectrochemical approaches enable energy storage in the form of transportable fuels.

Given the enormous efforts devoted to understanding semiconductor physics over the last four decades, it might be expected that semiconductor photoelectrochemistry would be a mature field and that optimised design of semiconductor interfaces for any of the above applications could be relegated to engineering practice. Indeed, the large body of information regarding semiconductor properties has had a major impact on the development of semiconductor photoelectrochemistry. However, most of this basic knowledge pertains to bulk properties and transport phenomena. Relevant as this information is to the above applications, it is the surface (photo)chemistry that is ultimately responsible for interfacial charge transfer and energy transduction, and our basic understanding of this is still evolving. The small number of reactive states at interfaces and the difficulties in separating surface from bulk observables have impeded progress. Despite these difficulties, significant advances have recently been made. We are rapidly coming to an understanding of the primary processes at a level rivalling homogeneous electron transfer in solution. There are, however, distinct features to the heterogeneous electron-transfer problem. The abrupt change in the dielectric medium, as defined by the interface, imparts interesting complexities to the problem. In addition, the reaction coordinate involves highly mobile states (charge carriers) and high fields (10^4 – 10^5 V cm⁻¹) that affect transition probabilities.

This chapter reviews the methodologies developed over the years to tackle various aspects of surface photoelectrochemistry. Section 2.2 gives an overview of all the photophysical and photochemical processes operative in semiconductor systems, combining findings from solid-state physics and chemistry. For completeness, the effect of quantisation of the band structure is included. The basic principles are presented to enable a smooth transition from purely molecular to purely solid-state

descriptions of the interfacial charge-transfer process, and to cover the full spectrum of electronic density effects. Section 2.3 provides background with respect to the energetics of the process and an introduction to electrochemical and *in-situ* optical probes of the interfacial charge-transfer process. With these fundamentals in place, Sections 2.4 and 2.5 give the basic design principles for solar energy conversion and photocatalytic energy storage. The chapter ends with a summary of the fundamental processes determining the net efficiency of charge separation and energy conversion.

2.2 Photophysics of semiconductors and semiconductor particles

This section is intended to give the reader the background to understand the photophysical phenomena involved in solar photoconversion as discussed throughout this volume. Figures 2.1 and 2.2 show the different fundamental processes that follow light absorption. Since a semiconductor has a virtual continuum of levels, an eigenstate description of the light-absorption process is inadequate. One has to consider the dynamics that evolve from the initially prepared electron–hole carrier states created by the light field. The different pathways are common to all classes of semiconductor, but the carrier dynamics can be dramatically affected by the specifics of the system. Figure 2.1 shows two different limiting cases that differ with respect to the electronic density-of-states and the dimensionality of the system. For the bulk semiconductor case (Fig. 2.1), the photocarrier dynamics are depicted in the presence of a surface space-charge field. Figure 2.2 shows a quantised band structure representative of mesoscale semiconductor systems to illustrate the effect of reduced dimensions.

For the most part, different solar energy conversion strategies involve the separation of charge across an interface (Miller *et al.*, 1995). It is this step that transduces the light energy into electrical or chemical energy or stores the energy as electrical or chemical potential. Thus the effect of an interface on the carrier dynamics needs to be taken explicitly into account in this discussion. The different photophysical and photochemical pathways available for relaxation from the optically perturbed state are shown in both Figs. 2.1 and 2.2, with the interface prominently featured for this reason. Figure 2.3 shows the complete zoology of the different photoprocesses common to all semiconductor systems as a hierarchical tree of scattering events. The hierarchical scaling (Fig. 2.3b) is based on the approximate time scale for the various events as they occur after the optical preparation of the nascent state. The ordering and branching depends on the density-of-states for the electronic and nuclear (phonon/solvent) degrees of freedom that determine the coupling between states involved in the relaxation process, whether it be photophysical or photochemical.

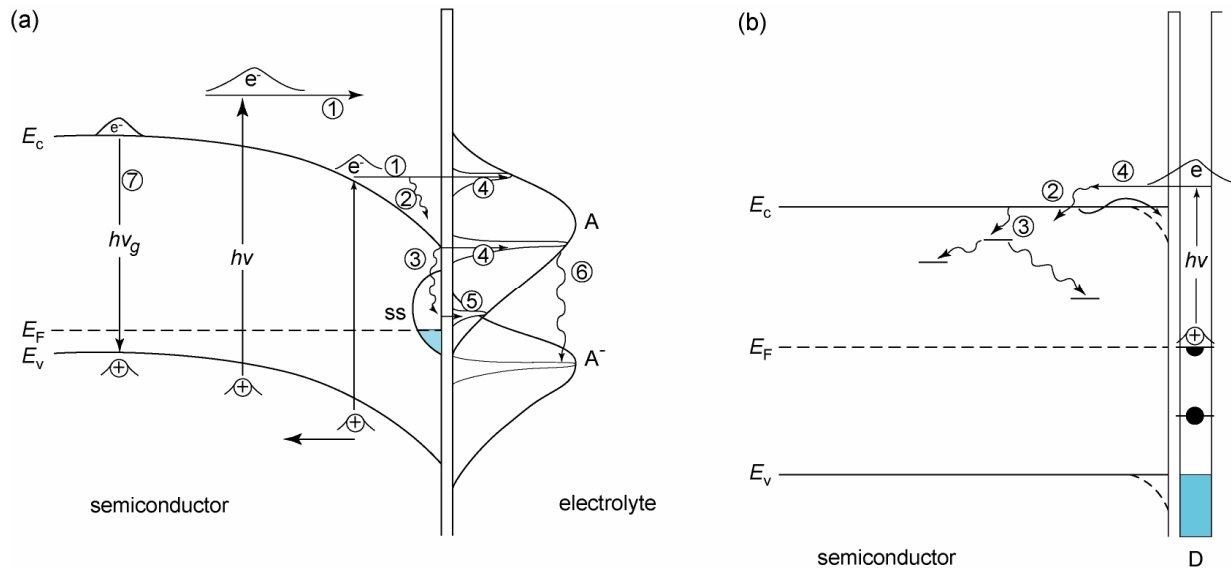


Figure 2.1 (a) Electron emission case for bulk semiconductors. The photophysical and photochemical processes for a *p*-type semiconductor with a liquid contact are shown. The different processes affecting the carrier spatial and energy distributions are numbered in approximate chronological order. ① labels the high-field transport in which the minority carrier is accelerated by the space-charge field to the surface and the majority-carrier to the bulk; ② refers to carrier relaxation within the band; ③ denotes surface-state trapping; ④ and ⑤ indicate interfacial electron-transfer from band and mid-gap levels to molecular acceptors (A) respectively; the term ⑥ is the solvent repolarisation process that ultimately localises the electron across the interface. The dynamic process ⑦ illustrates the carrier-density-dependent radiative recombination with emission of a photon $h\nu_g$. (b) Electron injection case. The reverse process in which the initial excited state is localised on a molecular donor (D). The labels refer to the same photophysical and photochemical processes as in (a). In this case, the electronic continuum plays the same role as the solvent relaxation (nuclear continuum) in localising the electron in the solid-state. The dotted lines at the surface represent the field that develops from the resulting parent cation. The electron has to escape this coulombic attraction to contribute to the photoanodic current or potential.

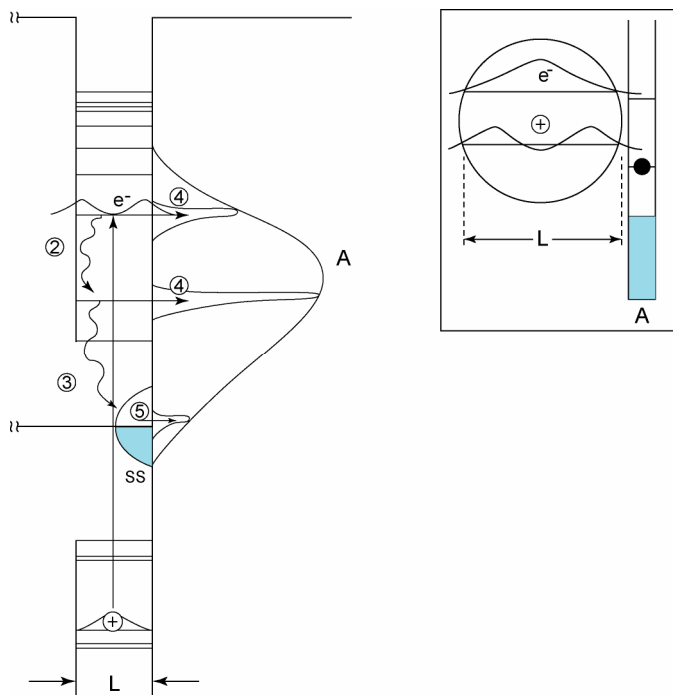


Figure 2.2 Electron emission from a quantum-confined system. The reactive state is the excited electron within a surface quantum well that is energetically degenerate with a distribution of molecular acceptors (A) at the interface. The inset depicts the electronic diagram for a quantum dot of acceptor A. The wavefunctions are drawn to illustrate a system in which the hole wavefunction is strongly mixed with the surface atoms. The step numbers denote the same physical processes as in Fig. 2.1.

The following discussion outlines the universal features and the distinctions between the bulk and nanoscale limits for these various pathways. Specifically, this section will emphasise the most recent advances in our understanding of relaxation and transport phenomena in semiconductors, as they pertain to photoinduced perturbations in the equilibrium carrier distribution. Under equilibrium conditions, the electron (n) and hole (p) carrier densities satisfy the relation (Sze, 1981)

$$np = n_i^2 \quad (2.1)$$

where n_i is the intrinsic carrier density, which depends on the semiconductor bandgap (E_g) and temperature. Optical excitation perturbs this relation. The relaxation of the system back towards equilibrium occurs through the various scattering and recombination processes shown in Figs. 2.1–2.3.

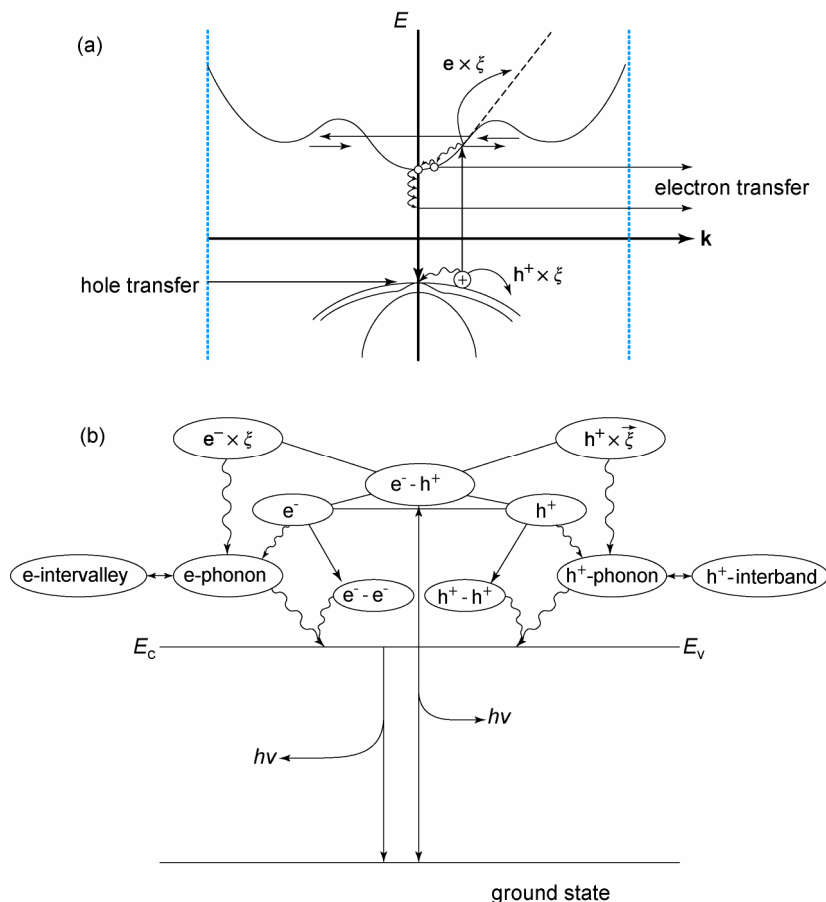


Figure 2.3 (a) Band structure diagram showing the same processes as in Fig. 2.1a. The field acceleration is depicted as $q \times \xi$ with ballistic motion within the central Γ valley indicated by motion (increased momentum) along the dotted line. In competition, intervalley scattering is shown along with carrier relaxation. The interfacial charge transfer is also indicated with pinholes in the k -diagram to illustrate the mixing with molecular acceptors; (b) Hierarchical scattering diagram. The left-hand side shows the electron-scattering processes; the right-hand side the hole-carrier dynamics. The initial process is the dissociation of the initially prepared states into free carriers. The carriers undergo field acceleration and subsequent carrier-carrier and carrier-phonon (intervalley and intravalley) scattering. Other processes such as carrier-acoustic scattering, defect scattering and impurity scattering do not affect the carrier energetics as significantly as the pathways shown. Both hot-carrier recombination and band-edge recombination are shown as $h\nu$ emission. These processes affect the carrier energy distribution and need to be taken into account in thinking about the electron-acceptor distribution and relative interfacial charge-transfer dynamics.

These processes govern all relaxation phenomena. Charge transport and the relaxation rates of the carrier populations to re-establish equilibrium conditions are normally described using the continuity and current density relations. For example, the one-dimensional (1-D) case for electrons under low injection is given by

$$\frac{\partial n}{\partial t} = G_e - \frac{\Delta n}{\tau_e} + nu_e \frac{\partial \mathcal{E}}{\partial x} + u_e \mathcal{E} \frac{\partial n}{\partial x} + D_e \frac{\partial^2 n}{\partial x^2} \quad (2.2)$$

where t is time, G_e represents the electron-generation rate, Δn is the excess carrier density, τ_e the lifetime of the excess electrons, $\mathcal{E}$ the electric field, u_e the electron mobility and D_e the electron diffusion coefficient. For uniform optical excitation, the generating function is defined by the optical conditions, *i.e.*

$$G_e(x, t) = j_{\text{abs}}(x, t) = j_o(t)(1 - e^{-\alpha(\lambda)x}) \quad (2.3)$$

where j_{abs} is the absorbed photon flux, j_o the incident light intensity, $\alpha(\lambda)$ the absorptivity at the excitation wavelength, and x the penetration depth from the surface. Using the explicit time dependence of the optical injection and various boundary conditions, one can solve eq. 2.2 for the parameter of interest. This conventional treatment works well for small perturbations near the band edges. However, this treatment considers only the spatial distribution of the carriers; there is no explicit dependence on the energy distribution of the carriers. As technology has evolved to shorter dimensions and higher speed devices, the relaxation of the carriers within the band has been found to have a pronounced effect on the carrier physics. Notably, the electron mobility and diffusion are highly dependent on the electron energy relative to the conduction-band minimum (CBM). For example, the interplay between field acceleration and scattering leads to an important effect known as the *velocity overshoot effect* in high-speed devices. Similarly, the dynamical processes of various photochemical channels are becoming better understood. It is clear that the reaction dynamics (Willig *et al.*, 1990; Lanzafame *et al.*, 1992 and 1994; Tachibana *et al.*, 1996; Hannappel *et al.*, 1997; Ghosh *et al.*, 1998; Martini *et al.*, 1998; and Asbury *et al.*, 1999) can compete with carrier-scattering processes (Schmittenmaier *et al.*, 1996; Diol and Miller, 1997) such that it is no longer valid to neglect the specific details of the carrier energetics. The above equation needs to be modified to specifically include an energy or $\mathbf{k}$ (momentum vector) dependence, as well as a spatial dependence in order to describe the relaxation and transport processes properly.

In the spirit of providing an updated account of the various photophysical and photochemical process to help drive paradigm shifts in solar energy conversion, we will emphasise the specific details of the carrier-relaxation dynamics with respect to

energetics, discussing the different photophysical and photochemical relaxation pathways in the chronological order shown in Figs. 2.1–2.3.

2.2.1 Field effects

One of the distinguishing features of bulk semiconductors is the formation of a space-charge region at the interface. The semiconductor interface is typically constructed between two dissimilar media that differ with respect to their electrochemical potential (Fermi levels) as isolated media. Once the system is in electronic contact, charge can flow across the interface in response to the initial difference in electrochemical potential. Under dark conditions, there is a net redistribution of charge that equilibrates the electrochemical potential across the interfacial boundary (Gerischer, 1970). In essence, electron exchange occurs and there is a net pumping of electrons under the initial difference in electrochemical potential, from higher-lying electronic levels to lower-lying acceptor levels. In an all-solid-state contact, this leads to the formation of a p – n junction. In photoelectrochemical systems, there is a liquid contact in which the ions in solution are mobile, unlike the impurity acceptor/donor states of the semiconductor. In this case, a junction is also formed, but it is similar to a metal/semiconductor Schottky junction in that there is an abrupt redistribution of charge on the electrolyte side of the contact, as there is with metal contacts, due to the mobile nature of the charges involved in both cases. The redistribution of charge leads to the development of a field that is a direct consequence of the difference in chemical potential and resultant built-in potential drop (V_{bi}) across the interface. The field and spatial redistribution of carriers and ions can be calculated from the continuity equations and the condition of charge neutrality. For an n -type semiconductor, the effective density n_s of electrons at the surface is given by (Sze, 1981)

$$n_s = n_o \exp - (qV_{bi} / kT) \quad (2.4)$$

where n_o is the majority-carrier density in the bulk ($n_o \cong N_D$, where N_D is the donor dopant density), q is the unsigned charge on an electron, k is the Boltzmann constant and T the temperature. A similar expression can be written for p -type semiconductor contacts. Typical values for the potential drop are on the order of 1 V, and eq. 2.4 shows that there is a significant depletion of the majority carriers. The majority carriers are pumped into the adjacent phase under the difference in electrochemical potential. Since the charge carriers in the liquid phase are mobile ions, the charge corresponding to the majority carrier accumulates at the surface in the formation of the Helmholtz layer; the charge balance is maintained by the ionised dopants in the

semiconductor. The lattice confines these ions such that a spatial gradient in charge develops and gives rise to a space-charge region, also referred to as a depletion layer, in the semiconductor. The spatial dependence of the carrier depletion within this region can be calculated from the distance dependence of the potential within the semiconductor.

The most important feature is the magnitude of the space-charge field. In the dark, field strengths are on the order of 10^5 V cm^{-1} to 10^6 V cm^{-1} for typical doping densities. The width w of the space-charge layer is determined by the potential drop across the interface

$$w = \sqrt{\frac{2\epsilon_0\epsilon_s}{qN_D} \left(V_{bi} - V - \frac{kT}{q} \right)} \quad (2.5)$$

where ϵ_0 is the permittivity of vacuum, ϵ_s the static dielectric constant and V any applied potential.

The charge Q_{sc1} in the space-charge layer per unit area of surface is equal to the total number of ionised donors in this region,

$$Q_{sc1} = qN_D w \quad (2.6)$$

The field magnitude can be calculated from the space-charge layer width and the potential drop across the interface. As can be appreciated from the above equation and a simple consideration of the charge density, space-charge widths depend on the semiconductor doping density. The width varies in the range of a few hundred Ångströms to micron-length scales, depending on the doping level. Herein lies one of the main distinctions between nanoscale materials (quantum dots, quantum wires and quantum wells). The dimension of quantisation is shorter range than the length scale of the field, so field effects are not nearly as important and in most cases are absent altogether for mesoscopic (nanoscale) semiconductor systems.

For bulk semiconductors, the space-charge field has a pronounced effect on the carrier dynamics in this region. The field magnitude is well in excess of that needed to overcome the coulombic attraction between the electron and hole carriers. This affects both the spatial distribution and transport properties of the carriers. There are two levels of coulombic interaction to consider. There is the attraction between individual electron-hole pairs that is responsible for what is referred to as exciton formation. In addition, there is the collective effect of the charge distribution integrated over the entire volume element. It is this latter coulombic interaction that is susceptible to space-charge field effects. The exciton binding energy is less than kT at room temperature such that this coulombic interaction does not represent a bound state. The

spatial envelope function of the electron and hole carriers becomes uncorrelated and the term *free carriers* gives a better description of the charged states. Despite the lack of correlation between the wavefunctions, the charged nature of the carriers and collective effect on local fields does affect the transport. In the absence of a field, the higher-mobility charge carrier (typically the electron) executes larger root-mean-square (rms) motion. In effect, the faster carriers move away from the slower counter charge, creating an effective charge separation. However, this effect is very short-range as the charge separation leads to a retarding field that prevents further charge separation. This effect is known as the *Dember effect*. It is this effect that determines carrier transport under zero-field conditions. Rather than the carrier transport being characterised by the mobilities of two distinct charge carriers, the diffusive motion is largely determined by the less mobile carrier. The ambipolar diffusion constant D_a that defines the spatial diffusion of charge carriers in this limit is given by (Sze, 1981)

$$D_a = \frac{(n + p) D_e D_h}{n D_e + p D_h} \quad (2.7)$$

where D_e and D_h are the electron and hole diffusion constants. In essence, the transport is determined by the slower carrier.

In the presence of the large fields present in the space-charge region, the collective coulombic interaction is overcome and there is a net separation of charge. In fact, the field magnitude is well in excess of the ambipolar fields and the carriers experience a large acceleration in the field region.

The effect of the space-charge field is two-fold. First, it leads to spatial separation of charge in which the minority carrier is driven to the surface by the electric field gradient. Second, the field acceleration imparts excess energy to both carriers. The details of the energy distribution of the minority-carrier arrival statistics at the surface reaction plane are important as the surface reaction dynamics depend exponentially on the energetics through the nuclear activation barrier terms (Sutin and Marcus, 1985; Miller *et al.*, 1995). The energy distribution and subsequent thermalisation relative to interfacial charge-transfer dynamics determine the branching ratios for interfacial charge-transfer from the different possible energy levels present at the interface. Some analytical treatments have been described to estimate the carrier transit time across the space-charge region (Jarret, 1981). However, these treatments only take into account the field effect through the carrier mobility and estimate an effective carrier velocity. From the space-charge width at a particular doping level, this approach gives an average transit time. No real information can be obtained about the energetics of the carriers subsequent to field acceleration, as the carrier-relaxation

dynamics cannot be added in an analytically tractable manner. The most useful information derived from such treatments is the fraction of carriers collected at the interface. This fraction η_{coll} can be estimated simply from the Gärtner equation

$$\eta_{\text{coll}} = 1 - e^{-\alpha(\lambda)(w+L)} \quad (2.8)$$

where L is the diffusion length, given by $L = [D\tau_a]^{1/2}$, where τ_a is the lifetime and D is the diffusion coefficient of the minority carrier. This expression defines the maximum charge-collection efficiency for a given wavelength in that it includes both the carriers generated within the space-charge region and those within a diffusion length of the junction, under low-injection conditions.

The maximum energy conversion efficiency can be estimated from this relation by integrating over the solar energy spectrum, explicitly incorporating the wavelength dependence of the absorption coefficient. Assuming that charge separation involves carriers at the band edges, the optimal energy gap is approximately 1.34 eV (single threshold absorber). In this case, the maximum solar energy conversion efficiency is 33% (no losses). In contrast, for interfacial charge-transfer occurring through hot-carrier processes (minimal minority-carrier thermalisation, *vide infra*), the solar energy conversion efficiency can approach 66% (Ross and Nozik, 1982). At the other extreme, charge transfer occurring through mid-gap states reduces the energy conversion efficiency to below 20%. The difference in the conversion limits reflects the amount of photon energy converted to heat in the solid-state lattice.

From the above, it can be appreciated that the details of the initial carrier distributions subsequent to field acceleration are important for fully optimising the energy conversion process. The most detailed study of the field acceleration process was conducted through a series of real-time measurements of the carrier transport directly in the space-charge region (Min and Miller, 1989 and 1990). From Poisson's equation for the space-charge field $\mathcal{E}$

$$\Delta\mathcal{E}(t) = \frac{q}{4\pi\epsilon_s\epsilon_0} \int_{-\infty}^0 n(x,t) - p(x,t) dx \quad (2.9)$$

there is no change in the magnitude of the electric field at $t = 0$ following an impulsive injection of electron-hole pairs. Both the electron, $n(x,t)$, and hole, $p(x,t)$, distributions overlap spatially. The action of the background space-charge field is to separate the electron-hole pairs created within the depletion region. This spatial separation of charge decreases the magnitude of the field and can be directly correlated to the spatial motion of the charge carriers through eq. 2.9.

The major technical challenge was to achieve sufficient time resolution to follow the field dynamics. Normally transient studies of electric fields and voltages using conventional electronics are limited by dispersion and stray capacitance in the leads, even with carefully designed waveguides, to bandwidths of 100 GHz or less. The corresponding picosecond time resolution is insufficient to follow the carrier motion across the space-charge field. However, by using an analogue of electro-optic sampling (Valdmanis *et al.*, 1982) it was possible to improve the time resolution to the requisite level. By taking advantage of the intrinsic electro-optic effect in non-centrosymmetric semiconductor crystals, an effective electrical bandwidth of ~ 10 THz was achieved (Min and Miller, 1989 and 1990). In contrast to electrical measurements, optical measurements of the field changes based on the electro-optic effect are only limited in time resolution by the frequency of the polar phonons that are displaced by electric field changes. For GaAs(100), this frequency response cut-off is at 8 THz. This bandwidth corresponds to 30 fs intrinsic time resolution, which is sufficient to follow even ballistic electron motion within the space-charge region. The key to these experiments was to avoid any electric contacts and to measure the field changes directly in the space-charge region through the evanescent field of a reflected optical probe beam in a pump–probe protocol (see Fig. 2.4). As the electron–hole photocarriers separate, the change in the electric field displaces the polar phonon modes, leading to a net change in the crystal birefringence that can be detected optically with polarisation-sensitive detection of the probe. In essence, as the charge carriers move through the crystal, the lattice deforms so that the carrier motion leaves a ‘wake’ behind it much like a boat speeding through water. The coupling of the electric field changes to the lattice phonons makes the carrier motion visible.

Figure 2.4 shows the main findings from the studies of carrier transport in GaAs(100)|oxide space-charge regions. Subsequent studies of metal|semiconductor Schottky contacts gave the same results and made it possible to examine a field dependence with an external bias (Cho *et al.*, 1990; Kersting *et al.*, 1993). The main feature is that the transit time across the space-charge region occurs on a 100 fs time scale for typical space-charge widths. A small fraction of the minority carriers have the right $\mathbf{k}$ vectors for ballistic motion to the surface reaction plane, whereas the majority generated within the space-charge region require at least one phonon-scattering process to direct the motion along the field direction. The observed time scale is shorter than carrier thermalisation, as will be discussed below. Thus the carriers arrive at the surface hot, that is, with excess energy transferred to them through the field acceleration. In principle, this energy acquired from the band bending is available for energy conversion as long as the charge can be stored as potential energy faster than it is lost to the lattice as heat (Boudreaux *et al.*, 1980).

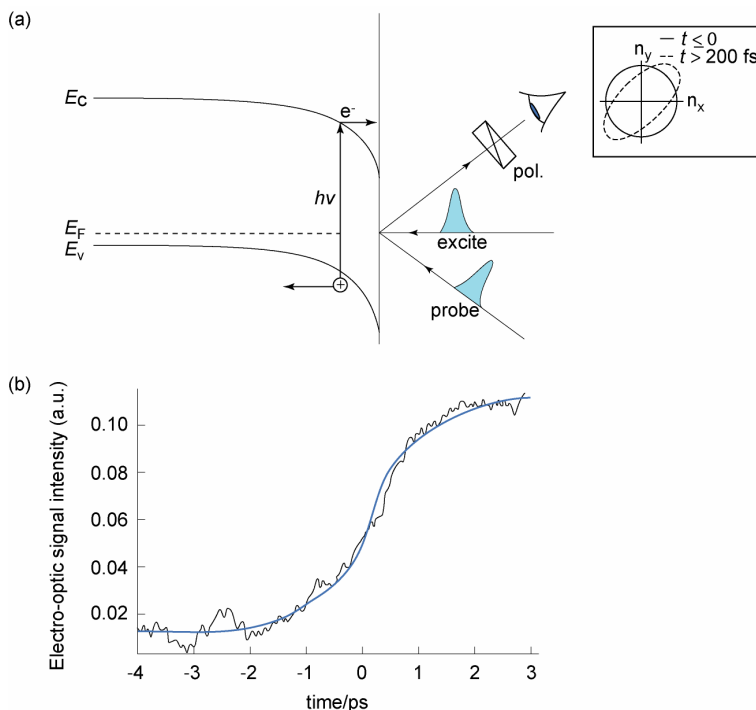


Figure 2.4 (a) Schematic diagram of space-charge electro-optic sampling. The excitation pulse injects photocarriers in the space-charge region that then separate under the influence of the field. The resulting field changes lead to a lattice deformation that can be probed by monitoring the change in polarisation of a reflected probe pulse through an analyser polariser (pol). The time-dependent change in crystal birefringence due to the carrier transport is shown in the inset. The full spatial motion can be resolved by continuously changing the time delay between the excitation and probe pulse; (b) Experimental data showing the field changes for GaAs(100) interface. The solid line is a fit to the data with a 200 fs time constant depicting the carrier transport to the surface region.

Qualitatively, the above transit time could be inferred from the carrier mobility to estimate the drift time in the presence of the field. However, the exact dynamics in relation to the carrier thermalisation are required for a determination of the initial minority-carrier energy distribution at the surface. The mobility is only accurate in describing diffusive processes, in that the mobility is related to the diffusion constant through the Einstein relation (Sze, 1981). Strictly speaking, a diffusive process for any transport process does not occur until several scattering processes lead to a ‘random walk’ (Rieger *et al.*, 1997). However, in hot-carrier phenomena the observed transit times are comparable or shorter than a single phonon-scattering event, and

diffusive motion in the presence of a field is thus not a good description of the process. The initial carrier motion is highly non-diffusive.

To model the carrier transport within the space-charge field of GaAs(100) more accurately, a full ensemble Monte Carlo simulation has been conducted (Zhou *et al.*, 1989). This calculation used a 10,000 quasi-particle basis, with the initial conditions modelling the experimental studies using short laser pulse injection, to enable the inclusion of carrier-carrier scattering. The magnitude of the field was updated in 1 fs intervals using a Poisson equation solver and the carriers were tracked in both $\mathbf{k}$ and $\mathbf{r}$ space with the inclusion of the full complement of scattering processes (carrier-carrier, intervalley, optical phonon, acoustic phonon and impurity) based on the GaAs band structure. The parameters were based on experimental measurements and detailed theoretical treatments of the various scattering processes, and checked for accuracy against a number of other experimental studies of carrier relaxation (Zhou, 1990). The predicted field dependence was found to be in reasonably good agreement with experiment, both in terms of predicted dynamics and field magnitudes.

Related analytical treatments have also been developed. However, the primary advantage of a Monte Carlo approach is the access it gives to the underlying microscopic details. Both the spatial and energy distributions of the carriers can be retrieved from the simulation. The main conclusions from this aspect of the work were that the carrier transport is strongly affected by intervalley scattering and carrier-carrier scattering. More than 50% of the field-accelerated energy was lost during the transit time, with the electrons becoming statistically trapped in the higher density-of-states L and X valleys. For electron minority carriers (*p*-type semiconductors), it is expected on the basis of this work that electrons would arrive at the surface with significant excess energy, scatter into the higher density X and L valleys in the band structure, and remain at higher energies than the conduction band minimum of the Γ valley for several hundred femtoseconds. Full relaxation to the conduction-band minimum should take picosecond timescales. The other important finding was that the carrier separation, under short optical pulse injection, generates a transient field that acts as a barrier to carrier diffusion into the space-charge region for carriers optical prepared outside this region. Thus, the optical measurements (Min and Miller, 1989 and 1990) provide information solely on the carrier transport in the space-charge region, which was the main intent of the studies.²

² The transient field leads to the counter-intuitive observation that the rise time in the transient photovoltage is slower at lower injection. At very low photocarrier injection, the barrier introduced by the transient field is insufficient to block diffusive motion of carriers outside the space-charge region, so diffusive

As with all simulations of this type, the dynamics are only as accurate as the starting basis of parameters. From the extent of agreement with experiment, the dynamics for the well-studied GaAs surfaces are considered to be accurate to within a factor of 2–3, significantly better than an order of magnitude estimate. The details will vary from semiconductor to semiconductor, depending on the band structure and the associated effective masses of the respective carriers, density-of-states, deformation potentials *etc.* Nevertheless, the general features should pertain to all classes of semiconductors. Namely, the space-charge field acts to separate the optically generated electron–hole pairs with the minority carrier being driven to the surface reaction plane. The minority carrier will arrive at the surface initially with excess energy. This generalisation, however, needs to be qualified. For large effective-mass carriers ($m_{e,h}^* > 1$), the field-assisted transport will be slower, reflecting the smaller mean free path for such systems. In this case, the mobility can be used to give a good estimate of the transit times. Thermalisation rates are faster, owing to the higher electronic density-of-states for large effective masses, and the minority carriers will lose most of the energy from field acceleration for such systems; that is, they will arrive at the surface at the band-edge energy.

It should be emphasised that the low light flux conditions of most solar cells create conditions in which there is a very low excess density of minority carriers. Thus, carrier–carrier scattering should be minimal once the minority carrier enters the space-charge region. This is further reinforced by the fact that this is a depletion region with virtually no majority carriers available for scattering interactions. Essentially only other photogenerated minority carriers are available and this scattering rate will be highest at the surface where the local density can be high (if interfacial charge-transfer rates are slow). In the absence of carrier scattering and assuming transit times faster than an appreciable number of phonon-scattering events, the carriers arrive at the surface with an excess energy corresponding to the degree of band bending. Even in the event of minority-carrier–carrier scattering, the energy remains within electronic degrees of freedom and is available for energy conversion. The main energy loss mechanism of concern for solar energy conversion is that of phonon scattering as this energy becomes lost entropically as heat into the lattice. Since phonon-scattering rates are surprisingly constant for a wide variety of materials (*vide infra*), it should be possible to estimate carrier transport and the energy distribution of the carriers at they enter the surface reaction plane using the methodology described above. The subsequent relaxation pathways and populations

components show up in the field dynamics. This effect must be taken into account in the study of interfacial charge dynamics that exploit space-charge separation of photocarriers.

of the different energy levels available to the minority carriers at the surface depend on the relative dynamics of the different competing processes.

To summarise this section, the effect of the space-charge field $\mathcal{E}$ on the photo-carrier distributions is shown schematically in Fig. 2.5. The main distinction between bulk semiconductors and mesoscopic systems is that the field is generally not directly involved in the separation of charge in quantum-confined semiconductor systems. For particles, in particular, any built-in fields due to surface charging are symmetric or nearly so and cancel as far as driving charge separation is concerned. The larger surface area of particle systems leads to charge separation as a consequence of either surface-state trapping or interfacial charge-transfer as the driving force. Once a carrier is trapped, a pronounced dipolar field develops that leads to some interesting consequences for the optical properties and coulombic barriers of semiconductor nanoparticles (Empedocles and Bawendi, 1997).

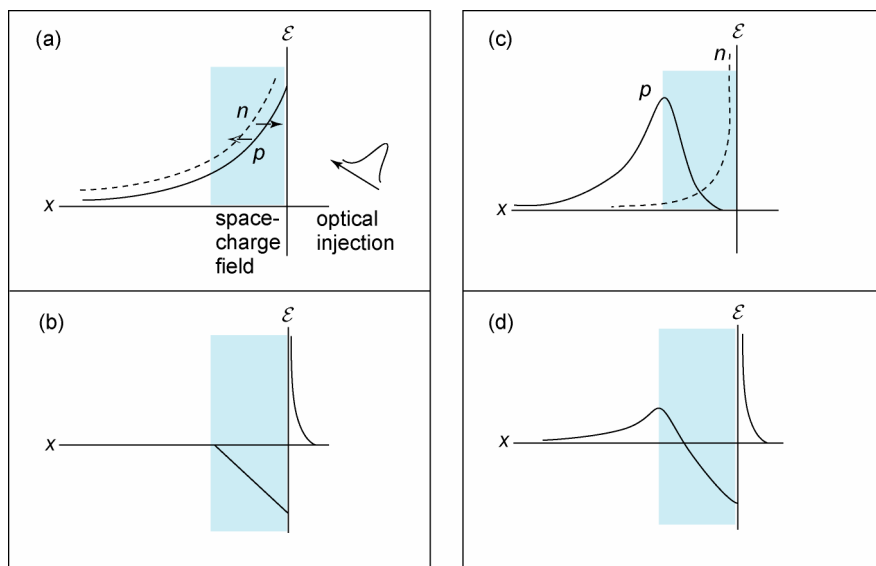


Figure 2.5 Schematic diagram showing approximate time sequence for the space-charge separation of the carriers. (a) Initial distribution. The photoelectrons and photoholes coincide spatially in each diagram. (b) The space-charge field lines prior to transport effects. (c) After 200 fs, the carrier distribution for a moderately doped p -type semiconductor has the minority electron carrier localised at the surface. (d) The field lines after carrier separation. There is a transient field line that creates a coulombic barrier to carrier diffusion into the space-charge region from the bulk. The blue area highlights the space-charge region.

2.3 Carrier relaxation

The optical excitation of electron–hole pairs represents a non-equilibrium state. The subsequent relaxation processes from the initial state includes both carrier–carrier interactions and coupling to the bath phonons. In some treatments, there is a distinction made between carrier–carrier and carrier–phonon interactions in which the latter is referred to as thermalisation. A two-temperature model is invoked in that the carrier–carrier scattering leads to a statistical distribution that can be described by an elevated electronic temperature, relative to the temperature characterising the lattice phonons (Schoenlein *et al.*, 1987; Schmittenmaer *et al.*, 1996). This two-temperature model is valid only if the carrier–carrier energy redistribution occurs on time scales much faster (>10 times) than relaxation into phonons. This distinction has limited value when there is not a sufficient separation in time scale to make a two-temperature model applicable. The main emphasis in this section is on the dynamics of the energy distribution of the carriers as this is most relevant to energy storage applications.

2.3.1 Bulk three-dimensional semiconductors

Optical excitation

In the event that the optical excitation involves above-band-gap light or field-accelerated carriers, the kinetic energy of the electrons is above that of the $\mathbf{k} = 0$ extremes of the valence band and conduction band and the carrier distribution includes hot carriers. The following discussion will chronicle the series of events that lead to the relaxation from this excess energy condition.

In the case of photon absorption, the incident light field drives a polarisation in the material that promotes an electron from the valence band to the conduction band. At the instant of creation of the electron–hole pair, the spatial envelope functions of the electron and hole wavefunctions overlap and have a well-defined phase relationship. This initial state preparation is different from an exciton in that the electron–hole pairs are formed within an electronic continuum of states and are therefore unbounded. In such circumstances, the use of dynamics to describe the state evolution is more appropriate than an eigenstate description with perturbative couplings between states.

The first process that occurs is the dephasing of the electron and hole wavefunctions. During the time interval that the electron and hole wavefunction have a degree of spatial overlap, there is an extremely rapid electron–hole scattering

process that leads to a broad distribution of initial energies. Femtosecond studies of radiative recombination using upconversion methods (Elsaesser *et al.*, 1991) and time resolved photoemission (Schmuttenmaer *et al.*, 1996) have found a broad carrier distribution on extremely short time scales. In fact, the narrow expected distribution for a $\Delta\mathbf{k} = 0$ allowed transition in direct-gap semiconductors has not been observed to date for even the highest time resolution (10 fs). The exact origin of this broadening is unclear at the time of writing, but it does significantly impact on the initial conditions normally assumed for the absorption of light by semiconductors. The simplest explanation is that there is a time-dependent carrier scattering rate. During the time interval that the electron and hole wavefunctions have a significant degree of overlap, the electron–hole scattering rate is orders of magnitude higher than at later times. Electrons within the valence band are able to scatter into the hole vacancy and concerted electron scattering to lower energy unoccupied states in the conduction band occurs to conserve momentum and energy. This process is most probably involved with the initial broadened distribution (femtosecond interaction times). Concurrent carrier scattering causes dephasing of the initial coherence imparted to the macroscopic material polarisation (Ueta *et al.*, 1986). The dephasing process has elastic and inelastic contributions from scattering off background carriers and phonon scattering. The relevant dynamics occur on 10 fs time scales at room temperature. Since this aspect of the carrier photophysics is related only to the phase of the macroscopic polarisation, there is no direct connection between dephasing and the carrier energetics. More important is the carrier–carrier scattering that leads to real population dynamics. These processes redistribute the energy among the carriers to create a Boltzmann distribution corresponding to an elevated electronic temperature with respect to the background lattice temperature. This latter process was thought to be much slower than that in metals as the relevant photocarrier and doping densities of semiconductors (10^{16} – 10^{18} cm⁻³) are typically four to six orders of magnitude lower than those of metals (10^{22} cm⁻³). However, the screening length in semiconductors is more than two orders of magnitude longer than in metals, with the result that the dynamics for this process are very similar (Fann *et al.*, 1992). For example, the screening length in Cu is approximately 1 Å, whereas for Si the screening length is on the order of 100 Å. This difference means that an electron in Si has an interaction volume four orders of magnitude larger than Cu. Carrier densities four orders of magnitude lower in semiconductors will exhibit the same carrier–carrier scattering rates as found in metals.

To provide some substantive details, *carrier–carrier scattering* is generally treated within a first-order time-dependent perturbation approach in which the transition rate from an initial $\mathbf{k}$ state to a final $\mathbf{k}'$ is given by (Reggiani, 1985; Zhou, 1989)

$$|\langle \mathbf{k} | \hat{H} | \mathbf{k}' \rangle|^2 = |V(\mathbf{g})|^2 \left| \int_{\text{cell}} u_{\mathbf{k}'}^*(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r}) d\mathbf{r} \right|^2 \quad (2.10)$$

where $|V(\mathbf{g})|^2$ is the Fourier transform of the time-dependent interaction potential with $\mathbf{g} = \mathbf{k} - \mathbf{k}'$. Integration of the periodic part of the Bloch wave functions $[u_{\mathbf{k}}(\mathbf{r}_i)]$ between the initial and final states gives the spatial overlap dependence and is strictly related to the non-parabolicity of the bands. This gives a single transition rate between $\mathbf{k}$ and $\mathbf{k}'$. Figure 2.6 shows the scattering process and total momentum phase available for carrier–carrier scattering schematically. The overall scattering rate needs to be integrated over all $\mathbf{k}$ space (re: $\mathbf{k}'$ as inferred from the figure). With this, the total scattering rate for electron–electron interactions (λ_{ee}) is given by (Reggiani, 1985; Zhou, 1990)

$$\lambda_{ee}(\mathbf{k}) = \frac{nq^4\mu}{2\pi\hbar^3(\epsilon_0\epsilon_s)^2} = \int \frac{g}{\beta_s^2(g^2 + \beta_s^2)} f(\mathbf{k}')^3 \mathbf{k}' \quad (2.11)$$

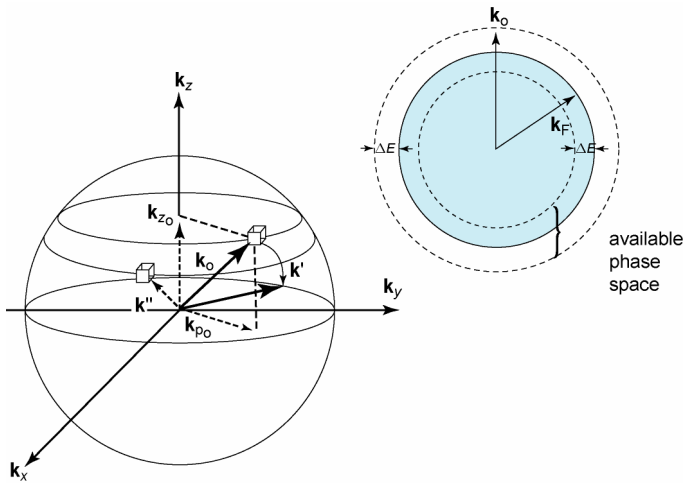


Figure 2.6 Electron–electron scattering diagram in $\mathbf{k}$ space for a parabolic band structure. The scattering of a carrier initially at $\mathbf{k}_0$ with a lower energy electron at the band edge (band edge, $\mathbf{k} = 0$) is shown with the hot electron being lowered to $\mathbf{k}'$ and the colder electron being elevated to $\mathbf{k}''$. The process has to conserve energy and momentum. The inset shows that the hot electron can scatter off any cold electrons up to the highest occupied states within the band. The available unoccupied states that conserve energy and momentum are indicated by the dotted line. The blue area shows the phase space available for scattering processes. As the electron relaxes to lower energy the number of electronic levels available decreases and so does the rate of electron–electron scattering. At some point electron–phonon scattering processes begin to dominate. The overall scattering rate is determined by the joint density of occupied and unoccupied electronic states.

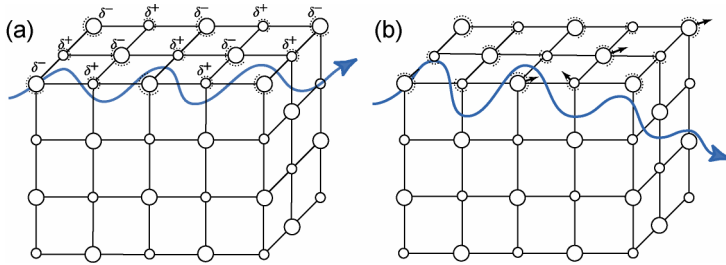


Figure 2.7 Artistic view of electron–phonon scattering. Lattice motions involving the displacement of polar modes can scatter the electron inelastically. The polar fluctuations create dipolar fields that can modulate the electron distribution. The electron responds to these stochastic fluctuations in local fields with a change in its energy and effective momentum transfer to the lattice. This process is depicted by comparing (a) and (b) to visualise the motion of the lattice atoms, leading to a change in direction or momentum of the electron from its initial path shown in (a).

where β_s is the inverse Debye–Hückel screening length, *i.e.* the screening length at which the dielectric response of the semiconductor cancels the charge-density fluctuations ($\beta_s = [q^2 n_o / \epsilon_o \epsilon_s kT]^{1/2}$, where n_o is the intrinsic electron density), μ is reduced mass (if the effective masses are different between $\mathbf{k}$ and $\mathbf{k}'$) and q is the fundamental charge. Assuming no change in effective mass, $g = |\mathbf{g}|$. The above scattering rate needs to take the electron distribution explicitly into account.

A similar relation can be derived for hole–hole and electron–hole scattering with appropriate changes to account for band structure. The essence of this mechanism is that changes in charge density following photoexcitation can interact coulombically with other carriers. Through this interaction, the excited state exchanges energy and momentum with the background carriers. The dynamics of this redistribution process depend on the carrier density and the screening length (which defines the volume element of $\mathbf{k}$ space available for scattering). As a rule of thumb, the carrier densities should be lower than 10^{16} cm^{-3} to avoid this energy redistribution process. At higher densities, the dynamics depend on the exact doping and photocarrier densities, as can be appreciated from eq. 2.11. However, the operating time scale is between 10 and 100 fs in the carrier range up to 10^{18} cm^{-3} . The carrier distribution becomes statistical on this time scale. Depending on the conditions, this process may have ramifications for the surface photochemistry. For example, an initial photoexcited electron distribution of 10^{17} cm^{-3} with 1 eV of excess energy relative to the CBM will scatter off colder carriers to an equilibrium distribution corresponding to an elevated electronic temperature of approximately 1000 K on a 100–400 fs time scale. Even though the initial distribution was 1 eV above the CBM, the electrons quickly attain a

statistical distribution near the CBM with the 1/e value of the distribution only 0.1 eV above the CBM.³

At lower carrier densities, carrier–phonon-scattering processes dominate the early time dynamics. Lattice deformations provide the coupling between different $\mathbf{k}$ states and enable exchange of energy between the lattice and the carriers. Figure 2.7 shows this scattering mechanism schematically. There are three different kinds of lattice displacements that affect different aspects of the carrier distribution and have different operating time scales. The highest frequency (fastest) lattice motions involve optical phonons with periods of modulation on the order of 100 fs (*e.g.* 8 THz frequencies for GaAs). The specific details of the lattice displacements or ‘deformations’ come into play. For example, asymmetric motions enable coupling of zone-centred Γ $\mathbf{k}$ states with the satellite X and L valley $\mathbf{k}$ states in GaAs. This process is referred to as *intervalley scattering*. The specific scattering rate (λ_{ij}) describing the process by which an electron in a valley i of energy E is scattered into a state in valley j of energy E' is given by (Fawcett *et al.*, 1970; Zhou, 1990)

$$\lambda_{ij}(E) = \frac{Z_j(m_j^*)^{3/2} \Xi_{ij}^2}{\sqrt{2\pi\rho\omega_{ij}}\hbar^3} F_{ij}(E, E') \times \left\{ \begin{array}{l} N_{ij} \text{ (absorption)} \\ (N_{ij} + 1) \text{ (emission)} \end{array} \right\} \quad (2.12)$$

where Z_j is the number of equivalent valleys, m_j^* the effective mass in valley j , ρ the density, ω_{ij} the intervalley phonon radial frequency, and Ξ_{ij} the intervalley deformation potential. The term N_{ij} is the intervalley phonon occupation number, given by

$$N_{ij} = [\exp(\hbar\omega_{ij}/kT) - 1]^{-1} \quad (2.13)$$

and $F_{ij}(\mathbf{k}, \mathbf{k}')$ is related to the spatial overlap factor (band non-parabolicity),

$$F_{ij}(E, E') = [E'(1 + \alpha_i E')]^{1/2} \frac{(1 + \alpha_i E)(1 + \alpha_j E')}{(1 + 2\alpha_i E)} \quad (2.14)$$

where α_i and α_j are the non-parabolicity parameters for valleys i and j , respectively and gives the energy conservation relation

$$E' = \begin{cases} E - \Delta E_{ij} + \hbar\omega_{ij} & \text{(absorption)} \\ E - \Delta E_{ij} - \hbar\omega_{ij} & \text{(emission)} \end{cases} \quad (2.15)$$

³ This process has a very pronounced effect on the carrier distributions and needs to be taken into account in the design of semiconductor/liquid contacts optimised for charge-transfer from band states. The acceptor distribution needs to be centred essentially at the band edges if this process is operative.

Asymmetric lattice displacements, as described by the intervalley phonon frequencies, lead to changes in $\mathbf{k}$ vector that corresponds to a different orientation with respect to the principal axes of the crystal that conserve energy and momentum. These scattering events are weighted by the appropriate Boltzmann factors for the phonon occupation and electronic overlap. Depending on the details of the band structure, this process can have some interesting consequences. Generally, the effective mass (band curvature) is larger (less) in these satellite valleys and the density of $\mathbf{k}$ states is higher in these regions of the band structure. Again, using GaAs as an example, the density-of-states (DOS) of the Γ valley is a factor of 10 less than the X and L satellite valleys. This difference in the density of $\mathbf{k}$ states enters into the overall scattering rates connecting the different features of the band structure. In this example, it is statistically ten times more probable for a scattering process to take a carrier from a low DOS region to the high DOS region. For this reason, the carriers become statistically trapped in the higher DOS region for extended periods of time. Essentially, the carriers spend 10 times longer (the ratio of the density-of-states) in the satellite valleys, weighted by the intervalley scattering time. There has been some disagreement in the literature as to the most accurate value defining intervalley scattering times⁴ and there is variability between different materials. Generally, the intervalley scattering is a fraction of the relevant phonon period driving the lattice deformation and as such is on the order of 10–100 fs. This process leads to a population bottleneck in the high density-of-states regions of the band structure.

The other phonon-scattering events involve $\mathbf{k}$ states and phonons in which the carriers remain within the same valley (conserve symmetry). These *intravalley scattering* processes are described by the rate (λ_{op}) (Kash *et al.*, 1985; Zhou, 1990)

$$\lambda_{\text{op}}(E) = \frac{\hbar^{1/2} \omega_{\text{op}}^{3/2}}{4\pi} \alpha_p F_{\text{op}}(E, E') \times \begin{cases} N_{\text{op}} & \text{(absorption)} \\ (N_{\text{op}} + 1) & \text{(emission)} \end{cases} \quad (2.16)$$

where $F_{\text{op}}(E, E')$ is again related to the non-parabolicity and has a similar form to eq. 2.14, and N_{op} is the Boltzmann-weighted optical phonon occupation number (eq. 2.13 with ω_{op} for the optical phonon frequency). The phonon-assisted scattering from E to E' must conserve energy and momentum as indicated for intervalley

⁴ The value of this constant is important as intervalley scattering of electrons to high density-of-states, low-mobility satellite valleys is a significant technical problem in high-speed semiconductor applications. This effect leads to a phenomenon known as ‘velocity overshoot’. High-mobility materials such as GaAs do not offer the previously anticipated advantages over Si due to this effect (Sinitsky *et al.*, 1997).

scattering in eq. 2.15. The term α_p is the Fröhlich coupling constant, given by (Fawcett *et al.*, 1970)

$$\alpha_p = \frac{q^2}{\epsilon_0} \left[\frac{m^*}{2\hbar\omega_{\text{op}}} \right]^{1/2} \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right] \quad (2.17)$$

where ϵ_∞ is the high-frequency dielectric constant and ϵ_s the static dielectric constant. The scattering requires some polar character in the lattice displacements, and is considered strong for $\alpha_p > 10$ and weak or negligible for $\alpha_p < 1$. If $\alpha_p \ll 1$, acoustic phonon-scattering dominates and the relaxation rate is much slower.

As with intervalley scattering, the dynamics become dominated by the highest frequency phonon modes with scattering times in the 50–200 fs range. Generally speaking, intervalley scattering rates are an order of magnitude larger than polar phonon scattering due to the higher density-of-states (factor of 10) satellite valleys that are involved. Intervalley scattering rates are on the order of 10^{14} s^{-1} in comparison to scattering rates of 10^{13} s^{-1} for intravalley polar optical phonon-scattering (Fawcett *et al.*, 1970; Zhou *et al.*, 1995). In both cases, the energy is being transduced from electronic degrees of freedom to mechanical degrees of freedom corresponding to the lattice. This aspect of the carrier relaxation is referred to as carrier thermalisation. The energy ultimately shows up as lattice heating once the intervalley and intravalley phonons further relax into the acoustical phonon branch. However, it is the intravalley, polar optical phonon-scattering process that is generally responsible for the final stage of carrier relaxation within the central Γ valley for direct-gap semiconductors, or within the lowest energy valley in the case of indirect semiconductors.

Since the phonon-scattering process really defines a rate, one must refer to a rate of cooling rather than a specific relaxation time. The cooling rate depends strongly on the density of electronic and phonon states. Thus, this rate will vary significantly with excess energy as the electronic DOS increases significantly in relation to the band edges. The cooling rate is also temperature-dependent through the dependence of the phonon occupation probabilities. The true lattice temperature dependence needs to be distinguished from dynamic, or transient, effects. The lattice phonon effective temperature increases during the phonon-scattering process, *i.e.*, the phonon distribution also changes. Under low-injection conditions in which minimal lattice heating occurs, cooling rates vary between 0.1 eV ps^{-1} and 1 eV ps^{-1} .

This condition pertains to most solar conditions and corresponds to picosecond time scales for electron distributions with 1 eV ($< 10^{17} \text{ carriers cm}^{-3}$) of excess energy to fully reach equilibrium with the lattice phonon temperature (3–10 ps for GaAs)

(Becker *et al.*, 1988; Zhou and Hsiang, 1990; Elsaesser *et al.*, 1991; Rosenwaks *et al.*, 1993). Under higher excitation conditions, the change in the phonon occupation is no longer negligible and carrier–phonon scattering processes in which a carrier is scattered to a higher energy state by absorbing a phonon, as opposed to phonon emission and carrier cooling, becomes an important process. At high enough excitation levels, a phonon population bottleneck is formed and the rate of carrier cooling by phonon emission equals the rate of carrier heating through phonon absorption in the scattering process. In this event, the overall carrier cooling is determined by the next relaxation phase in which optical phonons relax to acoustic phonons. The carrier cooling under these high excitation conditions can take 100 ps time scales or longer (Dassarma and Campos, 1994), and is ultimately limited by thermal diffusion and the boundary conditions for carrier generation. This *hot-phonon bottleneck* only operates under highly excited transient conditions. Under steady-state conditions, the true lattice temperature would have to be in excess of 1000 K to exploit this effect.

The last stage of the relaxation process involves the relaxation of the phonons emitted in the scattering process into acoustic phonons. This process is very similar to the relaxation of low-frequency modes in large molecules through collisional exchange. There have been only a few measurements of excited phonon lifetimes. Picosecond time scales are typically observed (Kash *et al.*, 1985) and lower limits for phonon lifetimes can be estimated by measurements of the linewidths in the infrared. The phonon lifetime is approximately an order of magnitude longer than the carrier–phonon-scattering time. The dynamics of the phonon relaxation do not directly affect the carrier distribution except under high excitation conditions when a hot-phonon bottleneck occurs in the carrier-cooling rate. In this case, once the excited phonons scatter into lower frequency acoustic phonons, the energy is truly in the last energy reservoir and can be considered an elevated lattice temperature (as opposed to an excited optical phonon distribution). The subsequent relaxation can be rigorously modeled as thermal diffusion (Elsayed-Ali *et al.*, 1987). Similar scattering rates to those in eqs. 2.12 and 2.15 can be derived for acoustic phonon scattering. The physics is the same and in most cases it is the intravalley and intervalley phonons that dominate carrier relaxation. Other scattering mechanisms such as ionised impurity and defect scattering do not affect the carrier energetics and are not considered here.

Space-charge field and surface effects on carrier relaxation

As far as photoelectrochemical processes are concerned, the most important physical process is the space-charge field effect on the carrier distribution. As discussed, the

field acts to separate the photogenerated electron–hole pairs and drive the minority carrier to the surface where it will have sufficient wavefunction overlap with molecular acceptors at the interface to open an interfacial charge-transfer relaxation channel. During this process, the minority carrier picks up excess energy from acceleration due to the force exerted on it by the field. As the carrier increases its energy, the various carrier relaxation pathways are also operative. The minority carrier can pick up as much as 1 eV of excess energy or more—the energy equivalent to the degree of band bending—from this process. The most important distinction between field-accelerated minority carriers and optically excited carriers is that carrier–carrier scattering should be negligible once the minority carrier enters the space-charge region, *i.e.*, this region corresponds to a depletion layer. The carrier density is far too low for majority-carrier scattering contributions and the photo-generated minority-carrier density must necessarily be low to avoid screening the field. Thus, only phonon-scattering processes will lead to energy loss as the minority carrier is accelerated to the surface. In contrast, the majority carrier is driven to the bulk and will experience the full spectrum of carrier–carrier and phonon-scattering processes.

The most significant relaxation process in terms of understanding the reaction branching ratios is the relaxation of the field accelerated minority carrier. The field further acts to localise the minority carrier in the surface region. For 1 eV of band bending and a space-charge width of 300 Å ($N_D \approx 10^{18} \text{ cm}^{-3}$), the 1/e point in the minority-carrier distribution is localised to within 10 Å of the surface. Thus the surface is expected to play a significant role in the minority-carrier relaxation.

In terms of predictive capabilities, this distinction creates problems as most of the studies of hot-carrier relaxation have been confined to bulk processes by the virtue of the experimental limitations associated with all optical methods. The majority of the carriers are generated and probed in the bulk of the crystal. Fortunately, in the last few years significant progress has been made in the development of femtosecond photoemission spectroscopy (Bokor *et al.*, 1986; Goldman and Prybyla, 1994; Haight, 1996; Schmuttenmaer *et al.*, 1996) which is sensitive to the near-surface carrier relaxation processes.

Figure 2.8 shows the experimental set-up. An above-band-gap, short laser pulse is used to optically excite electron–hole pairs with excess energy. The time evolution of the electron distribution is followed by the use of a second short laser pulse with sufficient photon energy to place the excited electrons above the electron affinity of the semiconductor. The optical generation of the carriers again is not selectively at the surface region of interest—but the probed states are.

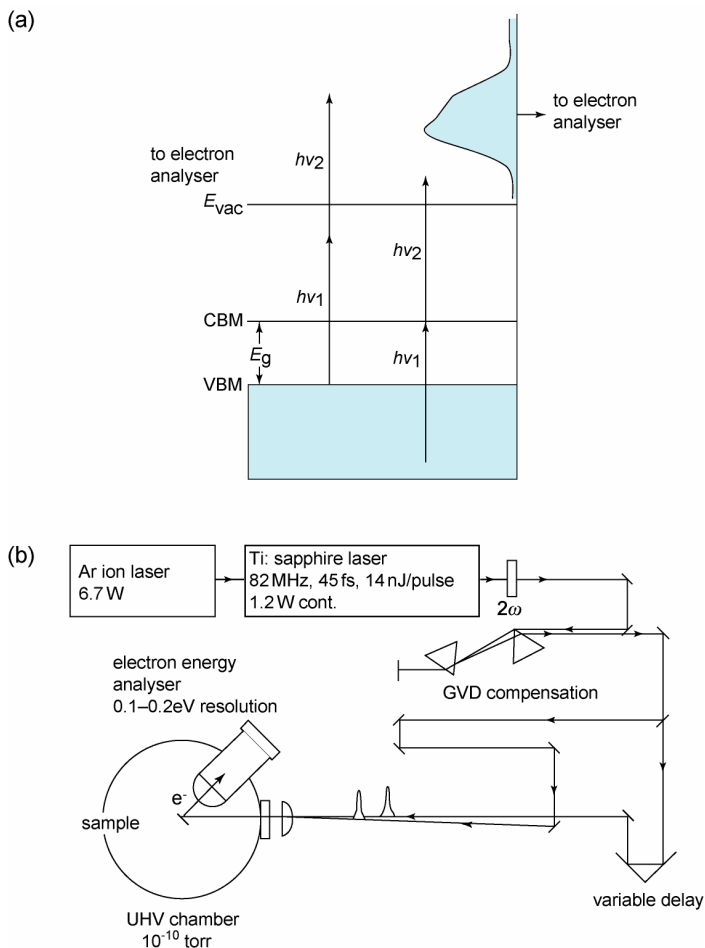


Figure 2.8 (a) Schematic diagram of electron photoemission from a semiconductor. One pulse ($h\nu_1$) prepares an excited electronic state, while a second pulse ($h\nu_2$) promotes the excited electron above the vacuum level. The electron is no longer a bound state and escapes to vacuum where the excess kinetic energy is measured with an electron spectrometer. The energetics of the excited electron distribution can be readily determined from the energy spectrum of the emitted electrons and the semiconductor electron affinity. Only those electrons within one mean free path make it out of the lattice potential. This approach provides true femtosecond time resolution, absolute energetics and high surface sensitivity. (b) Representative experimental set-up. The laser source shown is a Ti:sapphire laser that is frequency-doubled and split into two beams of equal intensity to provide an equal pulse correlation approach to measuring the photoelectron emission spectrum as a function of time delay between the pulses, produced by a motorised translation stage. The photoemitted electron spectrum can be measured with a time-of-flight or hemispherical energy analyser.

Only those electrons within the mean free path of the surface escape the surface potential and lead to photoemitted free electrons. The experiment is sensitive to distances on the order of 100 Å from the surface. Since interfacial electron transfer is also determined by electrons within one mean free path of the surface (*i.e.* virtually the same length scale), this experiment is ideally suited to probing the effects of the surface on the relaxation process.

The first experiments of this genre were concerned with relaxation near the CBM and surface band dynamics (Bokor *et al.*, 1986; Fann *et al.*, 1992; Haight, 1996). Recently, highly excited electron states were studied purposefully to make a direct connection to field-accelerated electrons of relevance to surface photoelectrochemistry (Schmittenmaer *et al.*, 1996). Well above-band-gap excitation pulses were used to generate electrons with excess energies of 1 eV to model field-accelerated electrons. Studies of device grade GaAs(100) for photoelectrochemical studies exhibited extremely fast electron relaxation. Electrons with excess energies between 0.3 eV and 1 eV relaxed on 10 fs timescales (see Fig. 2.9).

There was an issue concerning the carrier injection conditions with respect to the relative contributions from electron–electron scattering in relaxing the initial distribution. However, both *p*- and *n*-type materials showed the same dynamics. It was not until the excess energy was near the intervalley crossing point that the electron lifetimes in this energy range illustrated dynamics on the 100 fs time scale. The intervalley scattering to the higher density-of-states satellite valleys statistically trapped the hot electrons at energies corresponding to the minima of these valleys. To further check for surface contributions under the same excitation conditions, the a pristine, nearly atomically flat GaAs(100) surface was prepared by molecular beam epitaxy. With this ideal interface, the dynamics were found to be nearly an order of magnitude slower, as shown in Fig. 2.9. The faster dynamics observed for the device-grade surfaces could be recovered by using Ar ion bombardment to introduce surface defects. From this, it is apparent that a significant fraction of the carrier relaxation of conventional interfaces is due to surface scattering off defects. These must either be increasing the effective density of electronic states by mixing band states with surface states, or the deformation potential must have increased significantly (eqs. 2.10–2.16). The latter is a distinct possibility as the rms motion of the surface atoms is an order of magnitude greater than the bulk displacements (Chang *et al.*, 1999).

In addition, the polarity of the surface modes probably increases at a defect (either charge localisation in the midgap state or oxide bond formation would greatly increase the polarity of the modes (α_p) associated with the surface defect). The increase in polarity naturally leads to a larger modulation of the electron energy within the band and mixing of states for the same rms displacement.

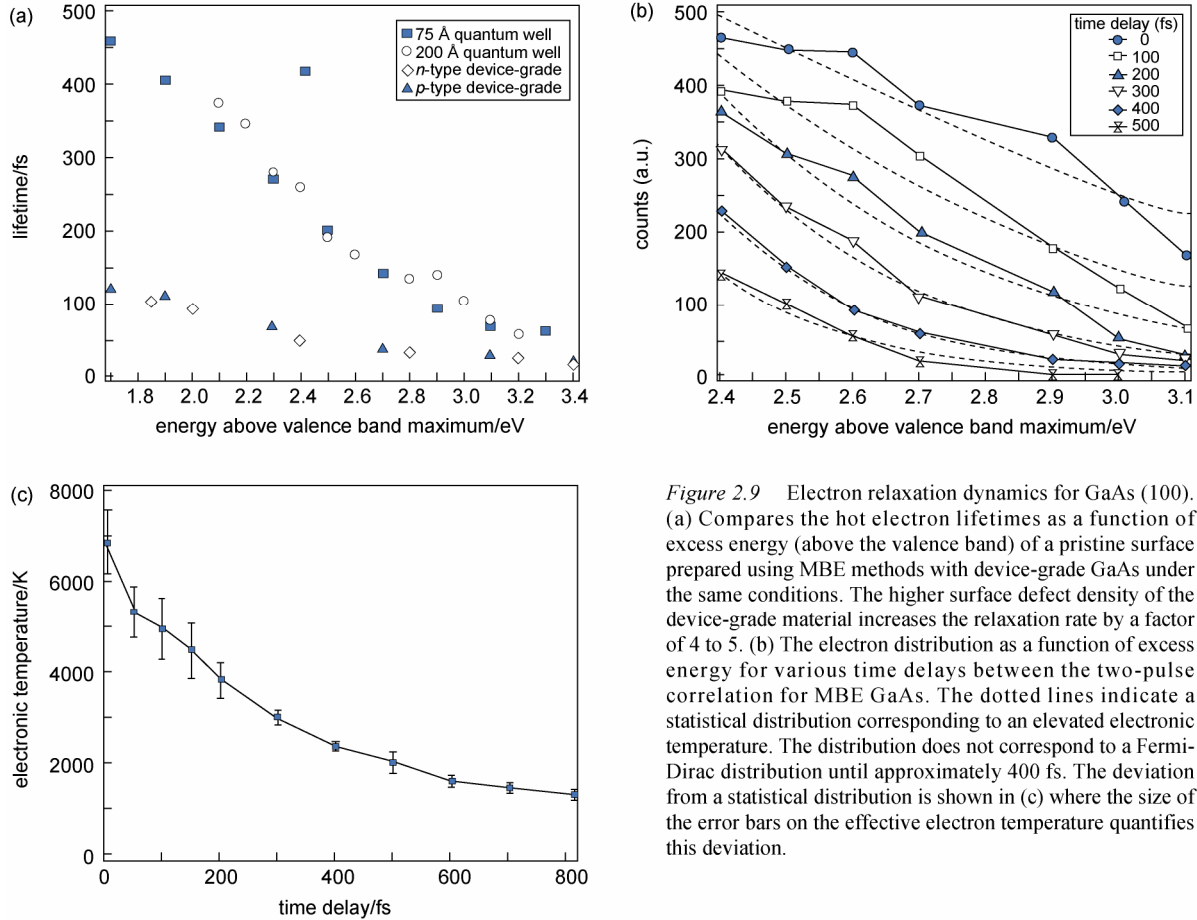


Figure 2.9 Electron relaxation dynamics for GaAs (100). (a) Compares the hot electron lifetimes as a function of excess energy (above the valence band) of a pristine surface prepared using MBE methods with device-grade GaAs under the same conditions. The higher surface defect density of the device-grade material increases the relaxation rate by a factor of 4 to 5. (b) The electron distribution as a function of excess energy for various time delays between the two-pulse correlation for MBE GaAs. The dotted lines indicate a statistical distribution corresponding to an elevated electronic temperature. The distribution does not correspond to a Fermi-Dirac distribution until approximately 400 fs. The deviation from a statistical distribution is shown in (c) where the size of the error bars on the effective electron temperature quantifies this deviation.

At the injection conditions employed, the observation is a convolution of carrier–carrier scattering and phonon scattering and both would be increased by the presence of surface defects. Lower injection conditions need to be achieved to completely eliminate carrier–carrier scattering from the dynamics and permit a definitive elucidation of the dynamics relevant to surface photoelectrochemistry under majority-carrier depletion conditions.

The main message from this class of experiments is that the details of the surface do affect the carrier relaxation. In the presence of surface defects associated with conventional surface preparation, the carrier relaxation in the surface region is exceptionally fast relative to bulk processes (10–100 fs dynamics). As can be seen by comparing the dynamics shown in Fig. 2.9, the effect of the surface is to increase the rate of relaxation and thermalisation. The asymmetry, more anharmonic character to the surface modes and increased mixing of states at defect sites all conspire to speed up the relaxation processes. With proper attention to surface structure, it is possible to intervene in the relaxation process and achieve carrier and phonon scattering rates that approach bulk processes. In this limit, 200 fs to picosecond dynamics define the operative time scales.

General features

The great variability of carrier cooling rates with injection level, density-of-states, and lattice temperature makes it difficult to offer simple rules of thumb. However, the microscopic features of the cooling process can be generalised. The maximum energy that can be lost in a phonon-scattering process corresponds to the highest frequency phonon participating in the process and must conserve momentum in the exchange. In this event, the scattering time is just the period of the high-frequency phonon. This can be used as an internal clock for thinking about the relevant time scales involved in intravalley thermalisation. For most semiconductors the highest frequency optical phonon has a cut-off between 5 and 8 THz (20 and 30 meV). To fully relax 1 eV of excess energy, there must be more than 30 phonon-scattering events with individual scattering events occurring at roughly 100 fs intervals. Without detailed information on the band structure, it should be expected that full relaxation of this amount of energy would take on the order of 3 ps, as observed experimentally in the bulk (Rosenwaks *et al.*, 1993). This picture is highly simplified as the excited carrier states are spatially delocalised and the band structure needs to be included explicitly in the relaxation (re: density of electronic states). However, the carrier wavefunction is only localised by the presence of lattice phonons. Provided there are no correlations between phonons on the length scale of the carrier mean free path, the electronic

wavefunction is altered by single-phonon scattering processes. Since the phonon modes are stochastic, uncorrelated processes, this simple approximation is sufficient for qualitative predictions, albeit providing only upper limits on relaxation rates.

Simple predictions of carrier relaxation dynamics are useful guides to understanding the various product-branching ratios of semiconductor photoelectrochemistry. If one considers the interaction time of the hot carrier distribution with molecular acceptors at the surface, an energy window needs to be defined. For example, if the full-width-half-maximum of an acceptor distribution is on the order of 0.1 eV, efficient charge transfer to this distribution requires charge-transfer times of less than 300 fs (electronic coupling between the band and molecular states in excess of 100 cm^{-1}). That is, the charge-transfer process needs to occur on time scales faster than the emission of three sequential 30 meV phonons. This estimate will be most accurate for excess energies where the density of electronic states is high and the relaxation is limited only by phonon scattering. For small effective mass carriers (*e.g.* electrons in GaAs), this excess energy range is on the order of 1 eV, whereas closer to the CBM, the density of unoccupied states become a limiting factor (~ 0.1 eV from the CBM) becomes a limiting factor and thermalisation slows dramatically, as discussed above. Picosecond dynamics for interfacial charge-transfer become a sufficient condition in this energy window.

2.3.2 Layered semiconductors: quasi-two-dimensional systems

As an intermediate step towards spatial confinement and increased quantisation of semiconductor band structure, there are bulk semiconductors that possess degrees of confinement due their highly anisotropic bonding. This two-dimensional (2-D) class of layered materials is characterised by complete termination of all valence electrons with in-plane bonding (Aruchamy, 1992). Only weak van der Waals forces hold the planes together in the crystallographic lattice. Representative materials of this class include SnS_2 , MoS_2 , MoSe_2 , and WSe_2 . For illustrative purposes of the general features, the SnS_2 crystal structure is shown in Fig. 2.10. Due to the strong covalent nature and π -character of the in-plane bonding, the effective mass of the carriers is generally small for $\mathbf{k}$ vectors in the plane, whereas there is very little overlap of atom-centred wavefunctions normal to the plane, as expected for van der Waals interactions. The effective carrier mass is large along this direction. The highly anisotropic nature of the carrier effective masses imparts interesting transport and physical constraints on the dynamics in these systems. In addition, it has been demonstrated that quite high quantum yields for photocurrent injection ($>80\%$) can be realised at

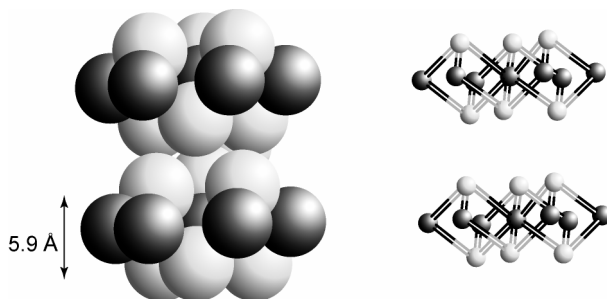


Figure 2.10 Quasi 2-dimensional layered semiconductors. The structure of SnS_2 is shown as a representative system. The large separation between the planes is due to the weak van der Waals forces holding the crystal together. The carriers are very strongly localised in the plane in these systems.

dye-sensitised interfaces using layered semiconductors (Parkinson, 1988). This is a remarkable observation as most dye-sensitised single-crystal semiconductors exhibit very low quantum yields (<3%) (Spitler, 1986; Miller *et al.*, 1995) for reasons that are not completely understood, as we discuss below. Only single-crystal silver halide and layered semiconductors have been found to facilitate charge separation and attain high quantum yields. The 2-D nature of these systems is thought to play a role in enhancing the photochemical processes at these interfaces.

It is only in recent years that studies of carrier relaxation dynamics have been conducted on these systems. The relaxation dynamics might be expected to be retarded relative to 3-D systems due to the reduced electronic wavefunction overlap and associated retardation in electron scattering for $\mathbf{k}$ space along the surface normal. In contrast, the electron relaxation dynamics for SnS_2 are found to be among the fastest of any material studied to date (Xu *et al.*, 1997), not excepting metals with high electron densities. Figure 2.11 shows the observed dynamics for electron relaxation, as derived from femtosecond photoemission experiments. The key observation is that the dynamics are in the 10 fs range and the excess energy dependence is linear rather than quadratic. That is, SnS_2 does not show the expected correlation to the electronic density-of-states in the conduction band. A new relaxation channel that is absent in non-layered materials has opened up in these materials.

The linear energy dependence observed in Fig. 2.11 (inset) is the hallmark signature of electron–plasmon scattering in layered materials (Xu *et al.*, 1996). In bulk 3-D materials, these many-body collective electron modes (plasmons) occur only at energies that are usually much higher in energy than the excited carriers (typically >3 eV) and resonant coupling is not possible. However, whenever such conditions exist, electron–plasmon scattering dominates as it only requires a single scattering

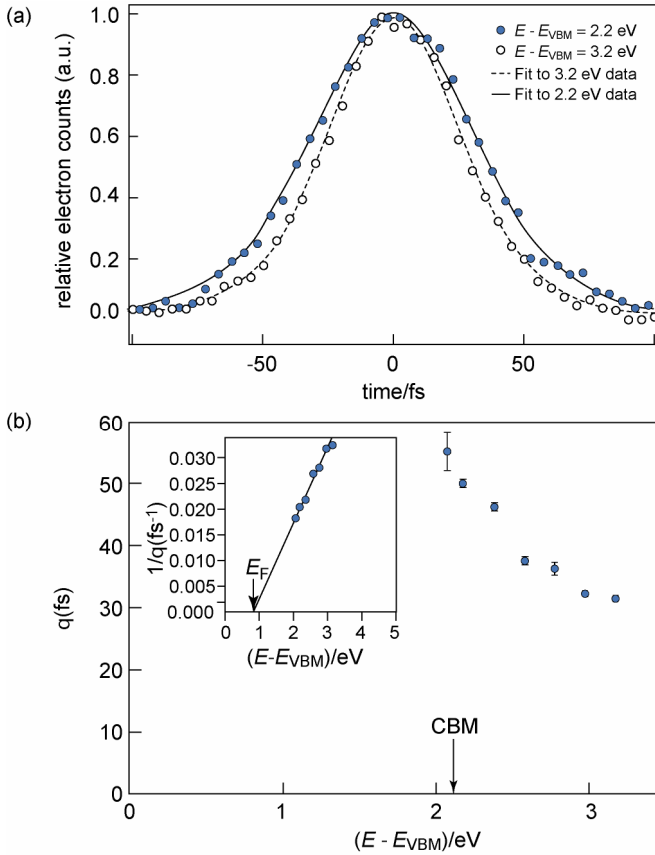


Figure 2.11 Electron relaxation dynamics in 2-D-layered materials. (a) The electron relaxation dynamics for SnS_2 are shown for two different excess energy conditions within 0.1 eV of the CBM (the bandgap is 2.1 eV) and approximately 1 eV above the CBM. In both cases, the relaxation is extremely fast and occurs on 10 fs time scales. The lines running through the data are best fits to single relaxation times of 40 fs and 60 fs for the 1 eV and 0.1 eV case. (b) The excess energy dependence corresponds to predictions where coupling to the broad plasmon band of these layered systems opens a new channel that significantly increases carrier relaxation above 3-D materials (compare Fig. 2.9).

event to distribute several eV of excess energy into a highly spatially distributed electron mode. In contrast, for layered materials, the plasmons are confined to each layer but new plasmon modes develop due to the coulombic interaction between layers (Hawrylak *et al.*, 1988). The plasmon, rather than having a single characteristic fundamental mode, now has significant energy dispersion with a plasmon band

extending from 0 to several eV in energy. For any excess energy state for the carriers in these systems, there will be an allowed plasmon mode available for scattering and the electron relaxation is accelerated by more than an order of magnitude. Typical phonon-limited scattering processes do not seem to factor into the relaxation dynamics at all—at least for SnS_2 .⁵

The energy can be viewed as still residing in electronic degrees of freedom and the relaxation of the plasmon into the lattice phonons should follow that described above, although the energy is not accessible through photochemical channels as the plasmon mode does not represent an elevated chemical potential. In this class of materials, the photoexcited electrons (and presumably hole carriers as well) which are available for reaction very rapidly lose energy to the plasmon band and relax to the CBM or undergo complete relaxation to the valence band on extremely fast time scales.

2.3.3 Quasi-one-dimensional semiconductors

In analogy to the layered 2-D semiconductors, it is also possible to produce one-dimensional (1-D) systems (*i.e.*, nanostructures with quantum confinement in two dimensions). This results in quantum wires (nanowires), quantum rods (nanorods) or nanotubes. Over the past decade this field has experienced exponential growth with about 1250 papers published in 2005 compared with none in 1994. Many important advances in the growth, characterisation and applications of 1-D systems have occurred and these are described in several reviews (Law *et al.*, 2004; Rao *et al.*, 2006; Lieber *et al.*, 2007; Robertson, 2007).

Some of these systems are an outgrowth of work on carbon-based fullerenes with the growth along one axis of a hemisphere of C_{60} (Fan *et al.*, 1999). Under proper growth conditions, single-walled nanotubes of several microns length and a few Ångströms radius have been grown over large areas. These systems can be considered cylinders of graphite with metallic or semiconducting behaviour depending upon their chirality.

In relation to the primary topic of this section, nanotubes are interesting structures to contemplate. In the semiconducting state, the gaps can range from 0.7 to 1.4 eV and hence could provide sufficient overlap with the solar spectrum for good collection efficiency. In the metallic state they could also serve as 1-D quantum wires forming a barrierless conduction path between donor and acceptor states and facilitate charge

⁵ Related studies of MoSe_2 and WSe_2 have also been conducted (Rettenberger *et al.*, 1997) but the emphasis was on carrier lifetimes rather than energy relaxation so a direct comparison is not possible.

separation for solar energy storage. We leave this as a potential topic for future investigation and include its discussion here for completeness.

2.3.4 Nanoscale-structured semiconductors

The above discussion pertains to macroscopic bulk semiconductors. With current methods of synthesis, arrested growth of colloids, and various film growth technologies such as molecular beam epitaxy and chemical vapour deposition, it has become relatively straight forward to fabricate complex structures on dimensions comparable to the effective de Broglie wavelength of the electron in the crystal lattice (Miller *et al.*, 1995, Chapter 6). The reduction in dimensionality of the semiconductor structure leads to an increase in the degree of quantisation along the confined axis. The different possibilities for confining the wavefunction by reducing one or all three dimensions are shown schematically in Fig. 2.12. Since the phonon wavelengths are also comparable to this scale, both the phonon branch and the electronic band structure become sparser with respect to level density along the confined direction of motion.

Spatial confinement has two interesting consequences. One is that the electron–hole binding energy increases and leads to enhanced exciton formation. An exciton is strongly analogous to a hydrogenic wavefunction, the hole carrier playing the role of the positively charged nucleus binding the electron carrier. The main difference between bulk and reduced-dimension semiconductors with respect to propensity for exciton formation is the increase in binding energy with reduced dimension. Spatial confinement leads larger wavefunction overlap (increased radiative recombination) but the bound nature of the state must be referenced to its binding energy relative to the background thermal energy. As a simple example, the exciton binding energy increases by a factor of four for a 2-D system as compared with a 3-D system.

The other natural consequence of spatial confinement and reduced dimension is the shift in the optical properties. As the structure is reduced in dimension, there is a shift to the blue with respect to the exciton absorption and onset of the band structure. The blue shift and increase in quantisation can be rationalised in terms of the dimension in relation to the Bohr radius of the exciton. Once the crystal dimension becomes smaller than the Bohr radius, the binding energy must increase, along with the degree of quantisation. The ability to control the optical properties and electronic structure of semiconductors by simply controlling the dimensions of the structure adds an important degree of control to optimising the system. Generically, the shift in transition energy with the spatial boundary conditions is conceptually equivalent to

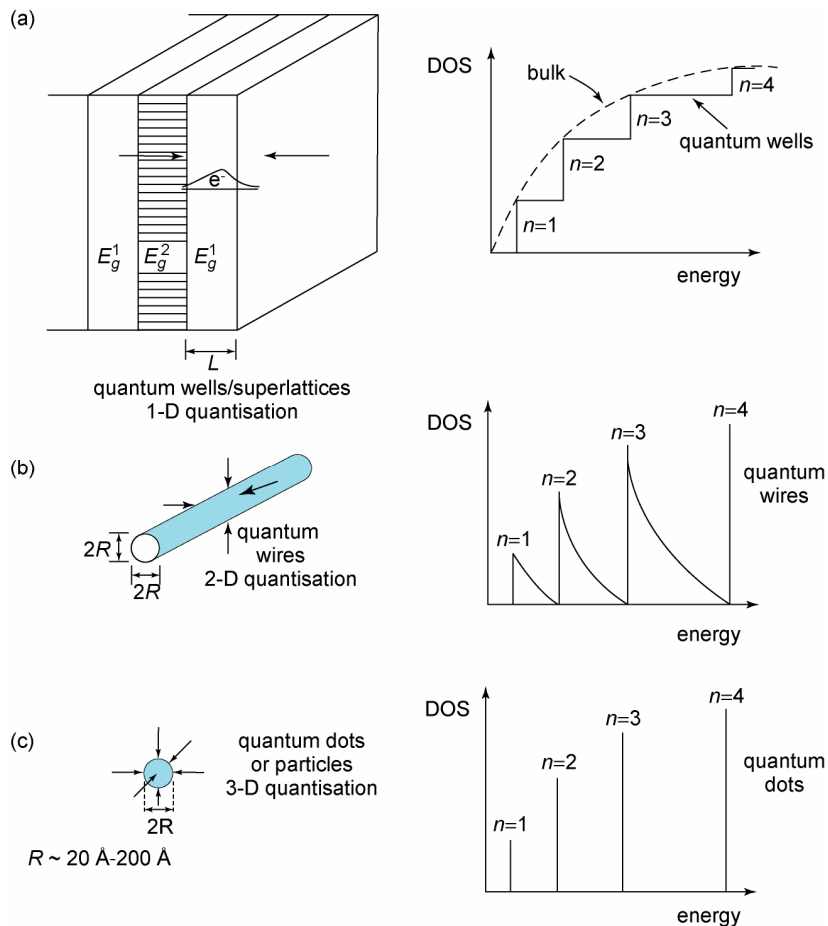


Figure 2.12 Schematic diagrams showing the different spatial confinement conditions that impose increased quantisation along the confined direction(s) in (a) one dimension; (b) two dimensions; (c) three dimensions. Quantum-confinement effects are observable once the reduced dimension becomes comparable with the de Broglie wavelength of the bound state. The scaling of the electronic density-of-states for different quantum-confined systems is depicted in the insets (after Chapter 6, Miller *et al.*, 1995).

the scaling observed in the simple quantum mechanical treatments of a particle-in-a-box. Specifically, the energy of the electron states for a 2-D structure (confinement along one direction only) with a finite barrier is given by (Miller *et al.*, 1995):

$$E_n = \frac{\hbar^2 k^2}{2m^*} - V_0 \quad (2.18)$$

where V_0 is the barrier height. The energy and number of levels within the well depends on V_0 . The exact solution is done graphically as a standard problem in quantum mechanics (Schiff, 1968). In order to calculate the shift in the exciton's optical transitions with dimension, the energy levels for the hole carrier states are needed, along with the density-of-states. The qualitative features of the density-of-states with reduced dimension are also shown in Fig. 2.12. For 2-D confinement, the DOS $[N(E)_{2-D}]$ is given by (Miller *et al.*, 1995)

$$N(E)_{2-D} = \frac{nm^*}{\pi\hbar^2}; \quad n = 1, 2, 3 \quad (2.19)$$

which should be compared to the bulk DOS for an isotropic band structure.

$$N(E)_{\text{bulk}} = \frac{\sqrt{2m^*} E^{1/2}}{\pi^2\hbar^3} \quad (2.20)$$

The hole states are more complicated as there are both heavy hole and light hole bands to consider. Nevertheless, conceptually it is very similar to the classic particle-in-the-box problem. The allowed optical transitions occur between energy levels in which $\Delta n = 0$, *i.e.* transitions between electron and hole states with the same quantum number. Since the energy levels of the electron and hole states scale the same with length, the shift in the exciton transitions show a very good correlation with the $1/L^2$ dependence expected from the simple particle-in-the-box picture.

For 1-D systems (which are confined along two directions), the exciton binding energy increases further. The effect of confinement on the electron's eigenspectrum, within a tight-binding approximation, is given by (Coulson *et al.*, 1962; Brus, 1986)

$$E_J \approx \alpha' + 2\beta' + \frac{\hbar^2 J^2}{8m^* L^2} \quad (2.21)$$

where the term α' is the self energy (upper valence orbital involved in forming the band), β' is the nearest neighbour resonance energy within a Hückel formalism, and J is the quantum number relevant to the confined direction.

The zero-dimensional systems referred to as 'quantum dots' involve arrested growth along all three crystal directions. Such growth conditions are relatively simple to achieve using limiting reagents and self-assembling procedures developed for colloids. These systems are intermediate between molecular and bulk semiconductor properties. Using the simplest zeroth order effective mass approximation (EMA), the exciton transition for 3-D spatial confinement is given by the relation for a particle-in-a-sphere as

$$E_n = \frac{h^2 n^2}{8m^* R^2} \quad (2.22)$$

where R is the radius of the sphere. Within the EMA but treating both the electron and hole wavefunctions, the energy of the first excited state is given by (Miller *et al.*, 1995)

$$E = \frac{h^2}{8mR^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8q^2}{\epsilon_2} + \left\langle \frac{q^2}{R} \sum_n \alpha_n \right\rangle \quad (2.23)$$

where α_n is the repolarisation or solvation energy

$$\left[\alpha_n = \left(\frac{\epsilon_2}{\epsilon_1} + 1 \right) (n+1) / \epsilon_2 \left(\frac{\epsilon_2}{\epsilon_1} n + n + 1 \right) \right]$$

and ϵ_2 and ϵ_1 are the dielectric constants for the semiconductor and surrounding medium, respectively. The last two terms are small, so a $1/R^2$ dependence is predicted. Experimental results do not show this size dependence, especially at small quantum dot sizes, and more rigorous models are required to reconcile the data. These models are discussed by Nozik in Section 3.2.2 of the next chapter.

The main difficulty with the synthesis of quantum dots is the attainment of monodisperse size distributions. Relatively good control of size has been achieved at the single 2–5 Å level (Empedocles and Bawendi, 1997). However, this degree of control still amounts to a 10% variation in radius and corresponding inhomogeneous broadening of the exciton transition and effective band-gap properties (eq. 2.22). The surface states have largely been passivated by encapsulating surfactants used to arrest the growth. The degree of surface structure variation is likely to be as inhomogeneously broadened as the exciton transition. This factor has not been well characterised and could lead to wide variations in photochemical properties that will be difficult to trace down until the photochemistry and surface-state distribution can be characterised at the individual particle level.

As discussed above, surface fields do not play as important a role in the photochemistry of these systems. The electric field gradients are not generally sufficient to completely separate the electron and hole wavefunctions. In the event of surface charging, the field effects are better treated as a perturbation on the wavefunctions and can be modelled as a first-order Stark effect. The effect is similar to a Franz–Keldysh effect for bulk semiconductors except that there is still significant hole and electron wavefunction overlap. The oscillator strength remains similar in magnitude, albeit the frequency shifts to the red as the electron–hole pair is more

polarisable than the filled valence band states. The effect of surface-state charging and associated Stark effect on the exciton transition has been observed at the single-particle level (Empedocles and Bawendi, 1997) and holds promise for unraveling some of the details of the surface-state distribution (via temperature dependence of the residence time in trap states).

For the fully relaxed, $n = 1$ exciton level, lifetimes of subnanoseconds to nanoseconds are observed for conditions in which there are few interfacial defects that limit the exciton lifetime (Adler *et al.*, 1997). The dynamics towards this fully relaxed excited state have not been as well characterised as bulk semiconductors however, the relaxation dynamics appear to be very similar. This may seem surprising, as the effect of increased quantisation has generally been thought to reduce relaxation rates. This conjecture is based on the expected density-of-states dependence of the scattering rates. Initial studies of carrier relaxation (2-D quantum wells and superlattices) found greatly reduced thermalisation rates. It was later shown that the retardation in the carrier cooling was due not to increased electronic quantisation but to increased quantisation of the acoustic phonon modes (Rosenwaks *et al.*, 1993). Basically, gaps are created in the acoustic phonon frequencies corresponding to in-phase and out-of-phase standing-wave conditions with the boundaries (Basseras *et al.*, 1994). This effect blocks spatial transport of the phonons out of the photoexcited region such that the lattice becomes hotter. This effect leads to an enhanced hot-phonon bottleneck. The excited acoustic phonons that arise from the relaxation process contribute to carrier heating. In other words, the hot phonon problem discussed above becomes exacerbated and carrier cooling becomes slower. Relaxation rates more than an order of magnitude slower have been observed in 2-D quantum systems due to this effect, under high optical injection conditions. Under low-injection conditions, in which the lattice temperature remains near ambient, the relaxation rates are virtually identical to the bulk values.

Apart from the enhanced hot-phonon bottleneck, the carrier thermalisation rate in 2-D systems is still expected to decrease, owing to the increased level spacing. Once the level spacing becomes greater than the highest frequency phonon involved in the thermalisation process, the mechanism would have to change from single-phonon to 2-phonon and higher phonon-scattering processes. That is to say, carrier scattering to a lower energy $\mathbf{k}$ state or exciton level has to be accompanied by the emission of two or more phonons to conserve energy and momentum (Boudreaux *et al.*, 1980). The higher order phonon emission process involves third, fourth and higher terms in the anharmonic expansion of the interaction potential and as such are far less probable events (the magnitude of the perturbation becomes smaller with increase in order). For example, a 2-phonon emission process is more than an order of magnitude less

probable than a 1-phonon process. This anticipated result has not really been observed, primarily due to the non-parabolic nature of the electronic band structure. For a 2-D quantum well problem, the electronic states are only quantised significantly along the surface normal. There is still a continuum of states parallel to the surface. The states in the plane, as defined by a parabolic band structure basis set, are significantly mixed with states along the normal. Thus, scattering can still occur to the continuum of $\mathbf{k}$ states in the plane. This effect and increased scattering channels to the in-plane momentum component is shown in Fig. 2.13. The magnitude of the coupling between states increases (on a per state basis) and essentially cancels the decrease in the electronic level density along the confined dimension. The increase in per state coupling with a decrease in density-of-states is a well-known effect for relaxation processes occurring within statistical limits (Miller, 1991). It should be stated that the effect of quantisation on carrier relaxation is still evolving and may be strongly dependent on interfacial defects, as discussed above.

There is one other important point to be made with respect to excited electronic state relaxation in quantum-confined systems. Based on the treatment of carrier relaxation given above, relaxation of electrons (above $n = 1$ levels) in quantum dots should show the greatest effect of spatial confinement. These systems exhibit the sparsest density-of-states and non-parabolicity should not factor in as all three dimensions are spatially confined. On this basis, highly excited levels should show very long lifetimes relative to the relaxation rates observed for bulk electrons with the same excess energy condition. To date, this effect has not been observed (Rosenwaks *et al.*, 1993). The problem is that the relations derived for periodic lattices are not invariant with dimension. At some length scale, a scattering approach to describe interconversion between electronic surfaces is not adequate and there should be a transition to molecular-like descriptions of the same process. In this connection, quantum dots can be viewed as large molecules. The internal conversion of excited state surfaces to the lowest excited state surface (*e.g.* $S_2 \rightarrow S_1$) for large molecules (more than 20 atoms) occurs on 100 fs time scales with few exceptions—very similar to phonon limited relaxation rates (Dlott, 1990; Miller, 1991). This extremely fast relaxation occurs even though the molecular electronic DOS is orders of magnitude less than bulk semiconductors (*e.g.*, a few electronic states/eV for molecules compared with 10^{18} /eV for semiconductor bands). The difference is that the spatial overlap factor of the electron and hole wavefunctions increases dramatically with spatial confinement and the per state coupling to the phonons (vibrations in the molecular case) increases at the same time. These two factors offset the decrease in the DOS. The coupling to vibrations is so strong in molecular systems that clear vibronic states within the same electronic level are observed in the optical spectra.

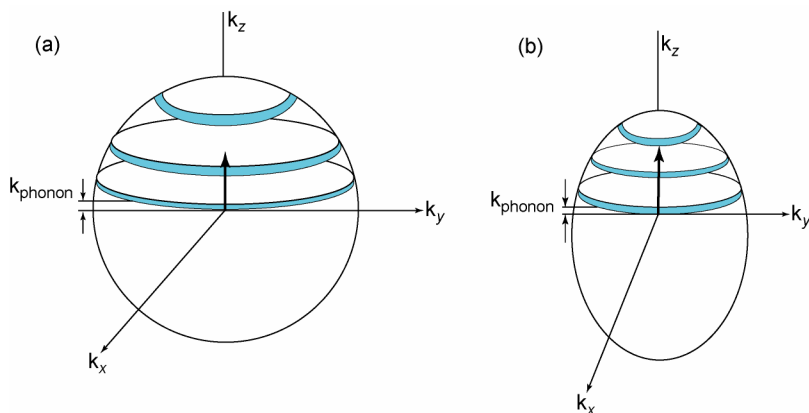


Figure 2.13 Schematic diagram showing the effect of the increased quantisation on the electron–phonon scattering rates. (a) For a parabolic band structure, once the level spacing is greater than the highest-frequency phonon able to conserve energy through relaxing from one level to another, the relaxation should slow down dramatically. Only higher-order interactions with the phonons will enable relaxation. This effect has not been observed to be a significant factor because the non-parabolicity inherent in most band structures strongly mixes the $\mathbf{k}$ -states along the confined direction with the continuum of states in the unconfined coordinates, as seen schematically in (b), which is a representation of the $\mathbf{k}$ -space curvature.

It is interesting to note that the relaxation of excited electronic states is so similar through such a large range of systems. The dynamics show almost universal behaviour. The more delocalised a wavefunction, the greater the number of relaxation pathways. The more localised the wavefunction, the stronger the per state coupling. The two effects appear to nearly cancel over a wide range of material parameters from large molecules, polymers, and nanoscale semiconductors to bulk crystals. Significant differences only occur when there are collective electron modes such as plasmons that provide new relaxation channels (increased relaxation) or the number of interacting atoms goes to the small-molecule limit where the level density finally dominates to give very slow relaxation rates.

2.3.5 Midgap state effects: surface-state trapping

Defects or impurities in the semiconductor crystal structure create electronic states in the gap region. In the case of impurities, the valence character of the impurity determines whether the level acts as an electron donor or electron acceptor state. In doping semiconductors, impurities are deliberately used to generate either donor or

acceptor levels within a few kT of the conduction or valence bands for n -type or p -type doping, respectively. However, unintentional impurities can create deep gap states that generally impart deleterious properties to the semiconductor. The most common type of impurity is a non-stoichiometric amount of one of the constituent atoms in the semiconductor (*e.g.*, As vacancies in GaAs or interstitial Ag in silver halides). There are also impurities from contaminants that become included in the crystal growth. Similarly, defects in the crystal structure create breaks in bonding patterns and change the degree of electronic coupling between atoms that lead to the formation of midgap states. The net effect of these midgap states is that they act as carrier trapping centres that increase resistive losses in device applications (heating, junction break down, inhomogeneous junction properties). Considerable effort has been expended in reducing the number of midgap states.

The effective cross section for trapping at such centres can exceed 10^{-16} cm^2 , which means that once a carrier spatially samples a defect site the probability for trapping is very high. The highly extended nature of the electronic wavefunctions and mobile nature of charge carriers makes the prerequisite level of purity extremely high. Impurity/defect levels less than $1/10^5$ are required just to keep the impurity density outside the mean free path of the carriers and carrier drift and diffusion raises the impurity requirement to much less than 1 ppm. Typical intrinsic defect densities of 10^{15} cm^{-3} are now readily accomplished in device-grade material, so that trapping in midgap states has been effectively mitigated in the bulk for most applications.

Surfaces represent a different challenge with respect to the propensity for the formation of midgap states. The very nature of the surface defines a break in the lattice bonding. The surface atoms are unterminated and the so-called 'dangling bonds' are energetically midgap and also represent reactive sites for contaminants (Heller, 1981). For surfaces that maintain the underlying bulk structure (simple termination), the surface atoms, by virtue of the missing adlayer, form a surface band that is midgap. It has only relatively recently been realised that most surfaces relax from the bulk structure to increase back bonding to the underlying layer. For example, surface relaxation at GaAs interfaces leads to increased coupling to the bulk and the surface bands are elevated to lie within the bulk bands (Duke *et al.*, 1980). Thus, the termination of the lattice by the surface does not intrinsically lead to the creation of midgap states, as previously thought. However, there is still a very high density of midgap states present at the interface. The areal defect density is typically in the range of 10^{12} to 10^{13} cm^{-2} for device-grade materials. Since the number of surface atoms is approximately 10^{15} cm^{-2} , this defect density represents up to nearly 1% of the surface sites, or an increase in areal density of more than three orders of magnitude from bulk values. The increase in density is due to a number of factors. Mechanical preparation

of the surface is one effect. Also the surface is in contact with the surrounding environment and is subject to the exchange of atoms, oxidation, *etc.*, that naturally create defects. The physics of trapping at the bulk or the surface are the same. The only difference is that the surface deformation potential is larger owing to the more anharmonic motion of the surface atoms relative to the smaller rms displacements of the bulk atoms/phonons. Thus, the surface-state trapping cross sections for the same class of defect is significantly larger than in the bulk. Due to the generally larger trapping cross section and much higher density of defect states present at the surface, most of the trapping occurs at the interface. For this reason, we will focus on surface-state trapping.

The relaxation of carriers into surface-state traps is an example of a nonradiative transition to a new electronic surface. There are many analogies of this process with electron transfer and nonradiative relaxation of photoexcited molecules. These analogies arise since carrier–carrier scattering no longer plays a role; the surface-states are localised defects and do not have travelling wave components that can mix with other band states. The relaxation process takes on a more localised basis to describe the electron probability distribution, reminiscent of a molecular scale problem. By definition, surface traps are energetically lower in energy than the CBM (or VBM in the case of hole trap states) by more than kT . The carrier must lose this excess energy through phonon emission. The trap cross-section and associated trapping dynamics depend on the energy gap between the trap state and the band. There is an energy gap law for analogous nonradiative molecular transitions that contains essentially the same physics. In the molecular case, the transition probability is weighted by the Franck–Condon factors (vibrational overlap in the two disparate electronic surfaces). In the case of solid-state trapping processes, one has the same consideration. If the trap level lies well below the band edge, a single phonon emission process is insufficient. One could use a multiphonon relaxation mechanism to attain the fully relaxed state, but such a description of this nonradiative process is an inaccurate description and would grossly underestimate the trapping dynamics. Again drawing on the molecular analogy, the defect itself will have a local phonon spectrum that is defined by the lattice deformation surrounding the defect. The transition probability to an upper level of the defect’s phonon spectrum depends on the equivalent Franck–Condon (FC) factor connecting the excited level of the defect’s local mode with that of the lattice phonon of the $\mathbf{k} = 0$ state of the band.⁶ The larger

⁶ To be correct, this interconversion of electronic states can occur at higher $\mathbf{k}$ states as well such that the overall rate would reflect the integration over the entire band. However, such states are still within the band

the energy gap the smaller the overlap of the nuclear wave functions for the two states and the smaller the transition probability.

Due to our limited ability to generate well-defined defects, a detailed exploration of the trapping process has not been conducted to date. However, a large number of molecular and polymeric systems have been studied and follow quantitatively the theory of nonradiative relaxation based on the above principles. The trapping rate should follow the relation for nonradiative relaxation of molecular states (Siebrand, 1967; Bixon and Jortner, 1968)

$$\ln \tau_{\text{trap}}^{-1} \propto -\frac{\gamma E_0}{\hbar \omega_{\text{op}}} \quad (2.24)$$

where τ_{trap}^{-1} is the effective nonradiative trapping time, and E_0 is the energy gap between the trap level and the band edge, given by

$$\tilde{\gamma} = \ln \left(\frac{E_0}{S_T \hbar \omega_{\text{op}}} \right) - 1 \quad (2.25)$$

The term S_T is related to the difference in nuclear displacements (ΔQ) between the ground state and higher-lying levels within the phonon progression of this electronic state. Conceptually, it is similar to the deformation potential described above. In molecular terms, eq. 2.25 is related to the Franck–Condon (FC) factors or overlap of the nuclear degrees of freedom in undergoing a transition from one electronic surface (band) to another (defect). The physics is the same; the main point is that the trapping cross section should depend exponentially on the energy gap. There are occasions where accidental degeneracies and larger FC factors occur in such transitions but generally the inverse energy gap law is observed with only minor corrections for a number of systems (Claude and Meyer, 1995). These processes have not been studied to the same level of detail as molecular processes but it is clear that trapping occurs fastest to shallow defects (Nirmal and Brus, 1999). These states often act as intermediate states to filling deeper levels within the gap.

Because of the large distribution of trap levels and difficulties in preparing a homogeneous surface, surface-state trapping is usually studied by characterising the surface recombination velocity. The details of the trapping dynamics can only be qualitatively determined as a product of an effective cross section and surface-state density. These experiments are generally conducted under zero-field conditions (*e.g.*

continuum and the trapped carrier would simply re-cross to the higher density-of-states within the band. Thus, the $\mathbf{k} = 0$ band state should be considered the doorway state to the trap electronic surface.

Forbes and Lewis, 1985) in which the surface is treated as an absorbing boundary condition on the photocarrier lifetimes. The normal assumptions give the expression (Sze, 1981)

$$\frac{dn}{dt} = G - \frac{Sn}{d} - R + \tilde{\mu}_n \mathcal{E}n \quad (2.26)$$

where d is the sample thickness, G and R are the bulk generation and recombination rates respectively, S is the surface recombination rate and $\mathcal{E}$ is included to take into account any internal field that develops due to differential trapping/transport of electrons or holes. The field $\mathcal{E}$ can be calculated using Poisson's equation (eq. 2.9). A similar expression applies to the hole carriers. The specific details and relative contribution of surface recombination depend on G . Typically a large laser spot size is used to irradiate the sample uniformly using strongly absorbed light to increase the surface contribution when the absorptivity becomes the relevant thickness parameter. The decay in carrier lifetime becomes dominated by surface-state trapping. The surface figure of merit is contained within S

$$S = \sigma N_{ss} v_{th} \quad (2.27)$$

where σ is the surface trap cross section, N_{ss} is the number density per unit area of surface-states and v_{th} is the thermal velocity of the carriers. The details of the trapping rates are contained within the trap cross-section and in principle should be defined with the energy gap law discussed above.

In comparing different studies of surface-state trapping, it should be kept in mind that the above simple treatment neglects finite trap lifetimes. It is assumed that once one carrier becomes trapped, the oppositely charged carrier becomes coulombically bound and instantaneously recombines nonradiatively with its charged partner. This assumption has been shown to impart limitations on the quantitative information that can be derived from such measurements (Shumaker *et al.*, 1992). Further, since the surface recombination velocity is a product of two unknowns (areal density and trap cross section), it is not possible to unambiguously test various tenets of nonradiative relaxation through the intermediacy of surface-state traps. Nevertheless, there are a number of *qualitative* features that can be gleaned from such studies. For example, a suitable high quality surface for most applications has a surface recombination velocity of less than 1000 cm s^{-1} ; whereas typical values for III–V surfaces are on the order of 10^3 to 10^5 cm s^{-1} . Using various estimates of the surface-state trap density, trap cross sections have been reported that vary between 10^{-12} cm^2 to 10^{-16} cm^2 (*e.g.* Miller and Richmond, 1997).

Surface trapping of charge carriers involves spatial transport to the surface and therefore the operative time scales must include a length scale for diffusive motion. This connection has been made extensively elsewhere (Lewis, 1991). As an example relevant to solar cell design, a space-charge field corresponding to 1 eV of band bending and 300 Å width confines the minority-carrier distribution to 10 Å of the surface. For a surface trapping velocity of 10^5 cm s^{-1} , the minority-carrier lifetime would be $\sim 1 \text{ ps}$. This lifetime is essentially thermalisation-limited. Recall from the above discussion of carrier relaxation that carrier relaxation near (within 0.1 eV) of the band edges occurs on picosecond time scales and is largely determined by phonon scattering. Once the carrier relaxes to the CBM, it becomes trapped almost immediately for surface capture velocities of this magnitude.

In terms of trap cross-section, this surface capture velocity gives an ensemble-averaged cross-section of 10^{-15} cm^2 for typical surface defect densities. Assuming that the structure of the trapping centre corresponds to a point defect such as a vacancy, this cross section is the same as the physical dimension of the trapping site. In other words, spatial sampling of the trap site would lead to trapping with unit probability within this picture. Note that the connection between structure and trap cross-section is an open issue. The real trapping process probably involves shallow traps that have larger dimensions (steps, dislocations) than the average trap cross-section. These shallow traps would act as intermediate states to deeper-lying states involving vacancies through energetically favoured hopping processes. The net effect, however, is the same. Surface-state trapping processes are generally very fast, and rapidly deplete free carriers from participating in energy storage. Resistive losses through carrier recombination also increase dramatically through the lowering of the effective barrier for charge recombination.

The above description primarily depicts surface-state trapping processes at bulk semiconductor interfaces. The photophysics is basically the same for reduced dimensional systems. The details that will differ will be the carrier thermalisation rate. In mesoscopic systems, the lowest lying bound state is not the $\mathbf{k} = 0$ state of the band but the $n = 1$ level of the exciton. The exciton wavefunction has appreciable overlap with the surface that defines the confining potential. In this case, there is no spatial transport required and significant mixing occurs in the nascent state. Carrier localisation at the surface in defects occurs on 100 fs time scales; a single phonon-scattering process is all that is required to displace the electron or hole from the fully extended excitonic function to one with surface character (Schoenlein *et al.*, 1993). Here, we are referring specifically to relaxation from the exciton level. Similar arguments could be made for the fully relaxed $\mathbf{k} = 0$ level of 3-D systems, except the

carrier spatial envelope function must also be near the surface (transport or $\mathbf{r}$ dependence needs to be included in the dynamics).

Rapid trapping by surface-states is a general feature that leads to energy losses, but this is not the biggest problem associated with surface-states. The inherent surface degradation due to photoinduced oxidation and reduction emanating from these states is a well-known problem (Heller, 1981); one that has limited the number of potential applications of semiconductor photochemistry in solar energy collection to this date. There have been two general schemes to solve this problem. One is to chemically modify the surface to passivate the surface-states. This approach only works if there is a relatively homogeneous distribution of defects that are amenable to surface adbond formation. Broad inhomogeneous distributions, oxidation-induced surface-states, and contaminants are difficult to displace and generally do not have sufficient mixing of electronic orbitals with the passivating layer to drive the levels out of the gap region. The other approach is to kinetically stabilise the interface by using charge-transfer processes to molecular states to regenerate the surface. In principle, it is possible to have an electron-transfer rate (*vide infra*) faster than surface-state trapping. The upper limit to both charge-transfer and surface-state trapping are very similar (Miller *et al.*, 1995) such that it is difficult to engineer a surface where hot carrier or band-edge charge transfer could completely dominate. In fact, for the majority of cases, surface-state trapping will dominate, in which case the trap states act as intermediates in the overall charge-transfer pathway. Under these conditions, kinetic stabilisation can still be achieved by making the charge-transfer pathways from the surface states faster than the other chemically deleterious side reactions leading to dissolution of the surface (Heller, 1981; Ryba *et al.*, 1993). The penalty is the effective bandgap for energy conversion has been reduced to some mean value related to the trap distribution with a corresponding decrease in conversion efficiency.

2.4 Charge transfer at the semiconductor–electrolyte interface

2.4.1 Energy levels at the semiconductor–liquid interface

A semiconductor is characterised by its energy bands, *i.e.* by the conduction and valence band and its Fermi level. In the bulk of the semiconductor, the position of the Fermi level depends on the doping. It is related to the electron and hole densities by

$$n = N_c \exp\left(-\frac{E_c - E_{F,n}}{kT}\right) \quad (2.28a)$$

$$p = N_v \exp \left(\frac{E_v - E_{F,p}}{kT} \right) \quad (2.28b)$$

where n and p are the electron and hole densities, and N_c and N_v are the density-of-states at the lower edge of the conduction band and the upper edge of the valence band, respectively. These functions depend on the effective mass m^* (N_c and $N_v \approx m^*/m_e^{3/2}$). $E_{F,n}$ and $E_{F,p}$ are the quasi-Fermi levels of electrons and holes. At equilibrium, where $np = n_i^2 = \text{const}$, we have $E_{F,n} = E_{F,p} = E_F$. Assuming an effective mass factor of unity, $N_c = N_v = 5 \times 10^{19} \text{ cm}^{-3}$. Also assuming that $E_c = E_F = 0.1 \text{ eV}$, the carrier density is about $n = 10^{18} \text{ cm}^{-3}$.

Taking a simple one-step redox couple as an example, the electrochemical potential of electrons is given by the Nernst equation

$$\tilde{\mu}_{e,\text{redox}} = \tilde{\mu}_{\text{redox}}^o + kT \ln \left(\frac{c_{\text{ox}}}{c_{\text{red}}} \right) \quad (2.29)$$

where c_{ox} and c_{red} are the concentrations of the oxidised and reduced components of the redox system, respectively. Usually, the corresponding redox potentials are given in relation to the standard hydrogen electrode (SHE) or the saturated calomel electrode (SCE) as a reference electrode. Using the theoretical absolute scale with a vacuum level as a reference point, the electrochemical potential of electrons in a redox system is equivalent to the Fermi level $E_{F,\text{redox}}$ (see Appendix 1A or *e.g.* Memming, 1994), *i.e.*

$$E_{F,\text{redox}} = \tilde{\mu}_{e,\text{redox}} \quad (2.30)$$

As explained in Appendix 1A, the absolute energy scale is related to the redox potential U_{redox} on the SHE scale by

$$E_{F,\text{redox}} = -4.44 \text{ eV} - qU_{\text{redox}} \quad (2.31)$$

At equilibrium, the Fermi levels are equal on both sides of the interface.

The actual position of the energy bands at the semiconductor surface can be experimentally determined by investigating the charge and potential distribution across the interface. The latter is composed essentially of the potential drop ϕ_H across the Helmholtz layer and ϕ_{sc1} across the space-charge layer below the semiconductor surface. Thus, the total potential difference across the interface is given by

$$U_E = \phi_{\text{sc1}} + \phi_H + C \quad (2.32)$$

where U_E is the electrode potential as measured between an ohmic contact on the

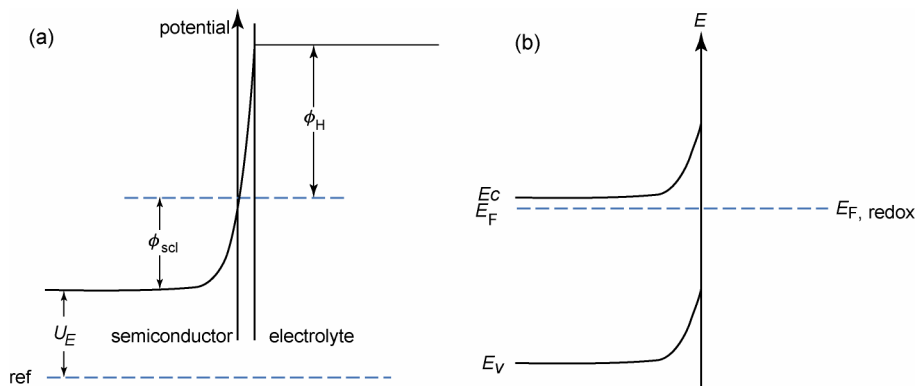


Figure 2.14 (a) Potential distribution at the semiconductor–liquid interface (ref: level of reference electrode). (b) Energy scheme of the same interface.

backside of the semiconductor electrode and a reference electrode (see Fig. 2.14a). The constant C is unknown and depends on the nature of the reference electrode. The potential difference ϕ_{scl} appears as a bending of the energy bands, as indicated in Fig. 2.14b. A potential drop across the Gouy layer (diffuse double layer) is neglected because there is usually a high concentration of ions in the supporting electrolyte. The double layer at the interface is the same as that found with metal electrodes. It can be formed either by adsorption of ions or molecules, by oriented dipoles, or by the formation of surface bonds between the solid and the species in solution. The counter charges on the solid side are not only located at the interface, as in a metal, but are also distributed over a finite distance below the surface (space-charge region); this is because the carrier density (usually in the range 10^{15} – 10^{19} cm^{-3}) is much smaller than in metals (where it is $\sim 10^{23}$ cm^{-3}).

Since the potential ϕ_{H} across the Helmholtz layer is unknown, it is impossible to theoretically predict ϕ_{sc} from energy considerations alone; rather the potential distribution has to be measured. Experimental information can be obtained by capacity measurements. The differential capacity of the space-charge layer below the semiconductor surface can be derived quantitatively by solving the Poisson equation. For doped semiconductors, one obtains the so-called Mott–Schottky equation

$$\frac{1}{C_{\text{scl}}^2} = \frac{2kT}{\epsilon\epsilon_0 n_0 q^2} \left(\frac{q\phi_{\text{scl}}}{kT} - 1 \right) \quad (2.33)$$

This relation is valid only for a space-charge region where the majority-carrier density is depleted with respect to the bulk density. The thickness of the space-charge layer, defined as $w = \epsilon\epsilon_0/C_{\text{scl}}$, decreases as doping increases. For a typical carrier

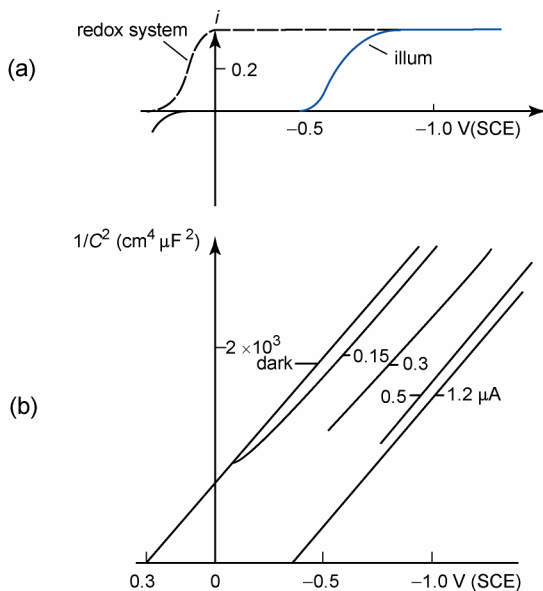


Figure 2.15 (a) Photocurrent–potential curve for $n\text{-WSe}_2$ electrode; (b) Mott–Schottky plots in 2 M HCl in the dark and under illumination (intensity given in photocurrents). Source: McEvoy *et al.* (1985).

density of $n_o = 10^{17} \text{ cm}^{-3}$ and band bending of $\phi_{\text{scl}} = 0.5 \text{ V}$, one obtains $w = 10^{-5} \text{ cm}$. The ‘dark’ line in Fig. 2.15 gives an example of a plot of $1/C_{\text{scl}}^2$ vs. electrode potential U_E . Since this Mott–Schottky plot is a straight line and its slope is identical to the theoretical value expected from eq. 2.33, it must be concluded that the potential across the Helmholtz layer remains constant. Extrapolation of the Mott–Schottky plot to $1/C_{\text{scl}}^2 = 0$ yields the electrode potential at which the potential across the space-charge layer approaches zero ($\phi_{\text{scl}} \rightarrow 0$). Accordingly, at $1/C_{\text{scl}}^2 = 0$, we find

$$\phi_{\text{sc}} \approx 0 \text{ and } U_E = U_{\text{fb}} \quad (2.34)$$

U_{fb} is called the flatband potential. In the above discussion, we assumed the energy bands to be pinned at the surface so any variation of the electrode potential leads to a change of the band bending, as illustrated in Fig. 2.16. Investigations of many semiconductor electrodes have shown that the position of the energy bands is independent of the doping, *i.e.* the energy bands of n - and p -type electrodes have the same position at the surface. In aqueous solutions, the potential across the Helmholtz layer is entirely determined by the interaction of the semiconductor and the solvent.

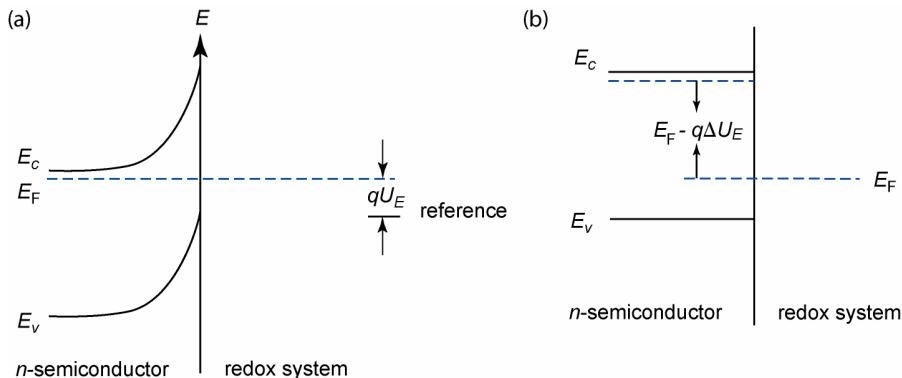


Figure 2.16 (a) Equilibration of Fermi levels across the semiconductor-liquid interface, showing band bending in the semiconductor space-charge (depletion) layer when the band edges are pinned; (b) Position of bands and Fermi level at flatband conditions as obtained under negative bias.

Figure 2.17 gives the energy position at the surface for several semiconductors in contact with aqueous solutions. In many cases, the flatband potential $\underline{U}_{fb}$, and consequently the position of the energy bands, varies with the solution pH because of protonation and deprotonation of surface hydroxyl groups, as especially found with oxide semiconductors, germanium, and some III-V compounds. In addition, anodic or cathodic prepolarisation of semiconductor electrodes sometimes leads to a change of ϕ_H . This has been interpreted by the formation of a hydroxyl surface during anodic polarisation and of a hydride surface at cathodic prepolarisation. For detailed information, see Gerischer (1970), Memming (1979), Nozik (1979), Morrison (1980), Pleskov (1980), Gomes and Cardon (1982) and Jägermann and Tributsch (1988).

Since the energy bands are pinned in aqueous solution, they also do not shift on addition of a redox system to the solution. Instead the band bending changes to maintain equal Fermi levels on the two sides of the interface at equilibrium. However, there are some cases where the energy bands are not pinned, but instead the semiconductor Fermi level is pinned. This frequently occurs in semiconductor/metal systems (Bard *et al.*, 1980; DiQuarto and Bard, 1981). In this case, changes in the Fermi level of the system, by change either in the redox system or the applied potential, shifts the position of the energy bands at the surface. Particularly in non-aqueous solutions, interaction between semiconductor and solvent is very weak so the addition of a redox system leads to a shift of bands. Thus, for example, the band positions at the surface of GaAs contacting acetonitrile or methanol depend strongly on the redox system (Ba *et al.*, 1993). The adsorption of a metallocene redox system causes an interaction between this redox couple and GaAs (Meier *et al.*, 1999).

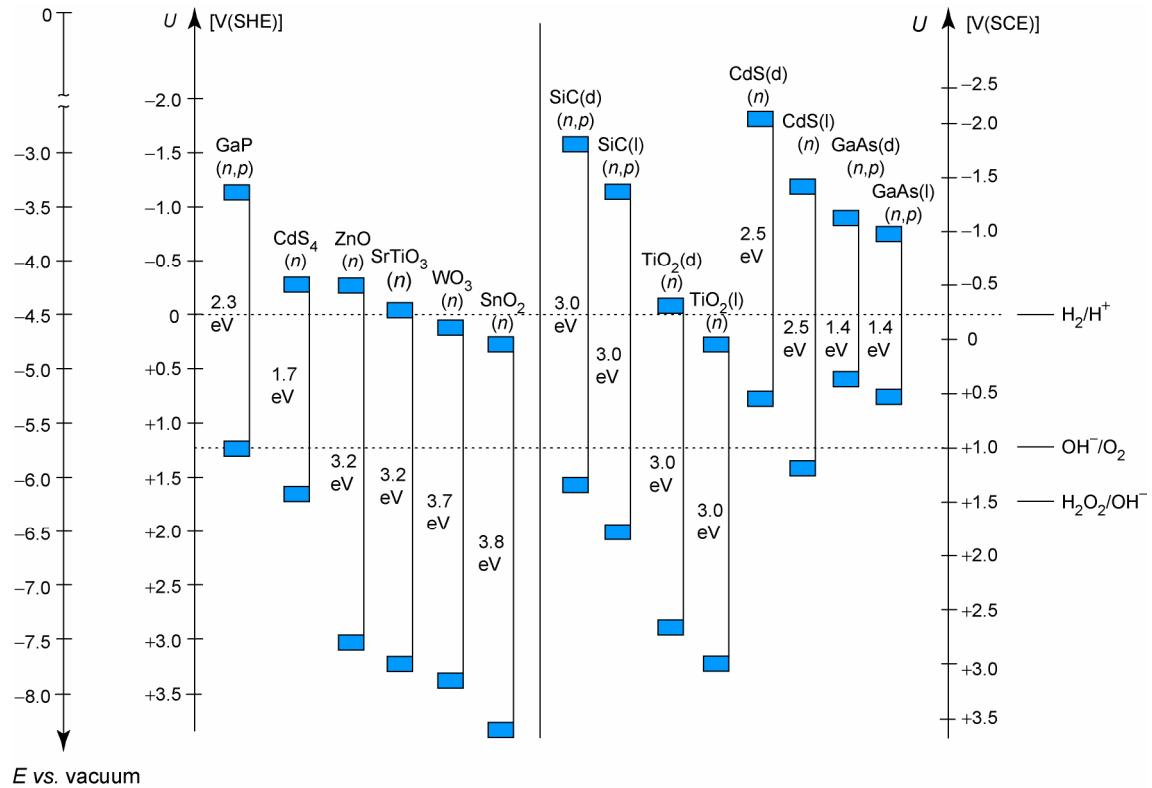
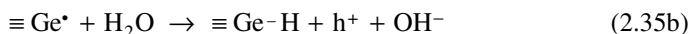
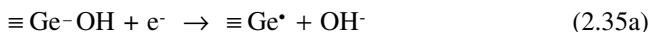


Figure 2.17 Position of energy bands of various semiconductors in the dark (d) and in the light (l) with respect to the SHE and SCE electrochemical scales U and the vacuum reference energy level E .

In 1981 it was reported for the first time that the Mott–Schottky curve measured with *p*-GaAs in aqueous solutions was shifted on illumination of the semiconductor (Kelly and Memming, 1981). This effect has also been found with many other *n*- and *p*-type semiconductors (Memming, 1994); an example is shown in Fig. 2.15b (McEvoy *et al.*, 1985). The shift increases at rather low intensity and saturates at higher light intensities. The flatband potential finally occurs around the onset potential of the photocurrent. This shift of the flatband potential is due to an unpinning of energy bands. This effect can be caused by trapping of photogenerated minority carriers in surface-states or by a very low rate of minority-carrier transfer, as found with *n*-WSe₂ (McEvoy *et al.*, 1985) and *n*-RuS₂ (Kühne and Tributsch, 1986). In both cases minority carriers accumulate at the surface, which leads to a change of the potential across the Helmholtz double layer, *i.e.* $\Delta E_{fb} = q\Delta\phi_H$. Band-edge unpinning can also occur if carrier inversion develops at the semiconductor surface.

It should be mentioned that an additional capacitance can occur in a limited potential range due to surface-states. Quantitative capacitance measurements with intrinsic Ge electrodes have shown that the density of surface-states was smaller than 10^{11} cm^{-2} after anodic prepolarisation (Brattain and Boddy, 1962). Since this number is much smaller than that found with semiconductor surfaces produced by cleaving in ultrahigh vacuum, the “wet” surfaces were claimed to be perfect. Interestingly, the Ge surface remained perfect even when the hydroxyl surface was converted into a hydride surface during cathodic polarisation according to the reaction (Gerischer and Mindt, 1966; Gerischer *et al.*, 1966).



In the potential range where the hydroxyl surface was converted to a hydride surface, a high density of surface-states was found which was related to the radical or to a dangling bond formed as an intermediate (Memming and Neumann, 1968). Additional capacitance has also been observed in Mott–Schottky plots for doped semiconductors. In most cases, however, correlation to surface-states was not unambiguously possible.

2.4.2 Majority-carrier processes

All electron-transfer processes must occur via one of the electronic bands or states of the semiconductor electrode. In some cases, the transfer does not occur directly at the

band edges but surface states are involved. The latter case will not be treated here. In aqueous solutions, most semiconductors undergo dissolution upon anodic polarisation. This is a valence-band process and it requires holes. At a *p*-type electrode the corresponding current rises exponentially whereas at *n*-electrodes a comparable current occurs only during light excitation. Oxygen formation instead of anodic decomposition has only been found with semiconductors of a large bandgap such as SrTiO₃ ($E_g = 3.2$ eV). Cathodic polarisation can also cause decomposition of some compound semiconductors such as ZnO and InP, but usually leads to H₂ formation. The latter reaction is always found to be a conduction-band process, *i.e.* a corresponding dark current can be observed with *n*-electrodes, whereas light excitation is required for *p*-electrodes.

In the case of redox reactions, either the conduction or the valence band can be involved, depending on the relative position of the standard Fermi level, $E_{F,\text{redox}}^0$, (or standard redox potential) of the redox system. This is illustrated for an *n*-type semiconductor for two different redox couples, one with a relatively negative standard potential (Fig. 2.18a), the other with a rather positive one (Fig. 2.18b), using the Gerischer model. It is assumed here that the electron transfer occurs without any energy loss (Franck–Condon principle). Accordingly, in the first case oxidation as well as reduction of the redox couple occurs via the conduction band (Fig. 2.18a) whereas in the second example the reaction is a valence-band process (Fig. 2.18b). The anodic current, arising from electron transfer from the redox system into the

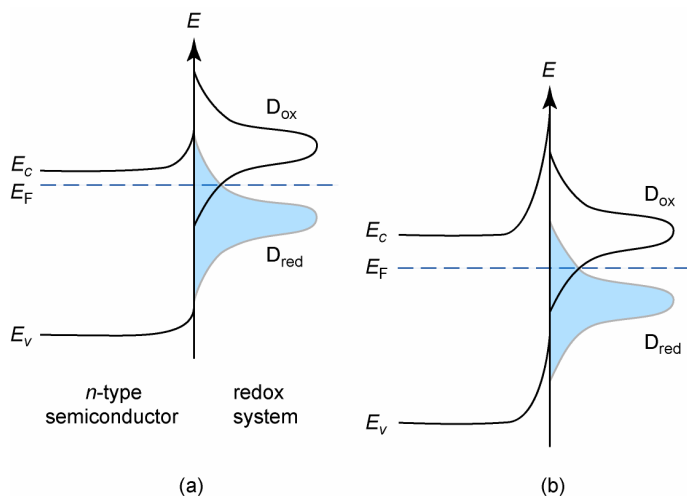


Figure 2.18 Energy levels at the interface of an *n*-type semiconductor and a redox system: (a) redox couple with a relatively negative standard potential; (b) with a rather positive standard potential.

conduction band of the semiconductor, is given by (Gerischer, 1961; Nozik and Memming, 1996)

$$i_c^+ = q k_c^+ N_c c_{\text{red}} \quad (2.36)$$

in which N_c is the density of states at the bottom of the conduction band and c_{red} the concentration of the reduced species of the redox couple, given in units of cm^{-3} . Thus, the rate constant k_c^+ has units of $\text{cm}^4 \text{s}^{-1}$ and can be expressed as the product of a maximum rate constant $k_{c,\text{max}}^+$ and an activation term (see also Section 2.3.5) below as given by

$$k_c^+ = k_{c,\text{max}}^+ \exp \left[-\frac{(E_c - E_{\text{F},\text{redox}}^0 - \lambda)^2}{4kT\lambda} \right] \quad (2.37)$$

where λ is the reorganisation energy. Since the conduction band edge remains fixed with respect to $E_{\text{F},\text{redox}}$ during polarisation, the rate constant and consequently the anodic current i_c^+ are independent of the potential. The cathodic current is similarly given by

$$i_c^- = q k_c^- n_s c_{\text{ox}} \quad (2.38)$$

in which c_{ox} is the concentration of the oxidised species of the redox system and n_s is the electron density at the surface, defined by

$$n_s = n_o \exp \left(-\frac{q\phi_{\text{scl}}}{kT} \right) \quad (2.39)$$

Here n_o is the electron concentration in the bulk. The rate constant k_c^- can be expressed by

$$k_c^- = k_{c,\text{max}}^- \exp \left[-\frac{(E_c - E_{\text{F},\text{redox}}^0 + \lambda)^2}{4kT\lambda} \right] \quad (2.40)$$

The cathodic current i_c^- varies with the electrode potential because n_s depends on ϕ_{scl} , and therefore on E_{F} , as illustrated by the dashed curve in Fig. 2.19. Analogous expressions are obtained for the valence-band processes.

According to eqs. 2.38 and 2.39, the cathodic current is proportional to c_{ox} and n_s . Provided that any potential variation occurs across the space-charge region, the cathodic current at an n -type electrode is expected to increase by one order of magnitude if the electrode potential is varied by 60 mV. In many cases the current was found to increase exponentially with the electrode potential, but the slope did not

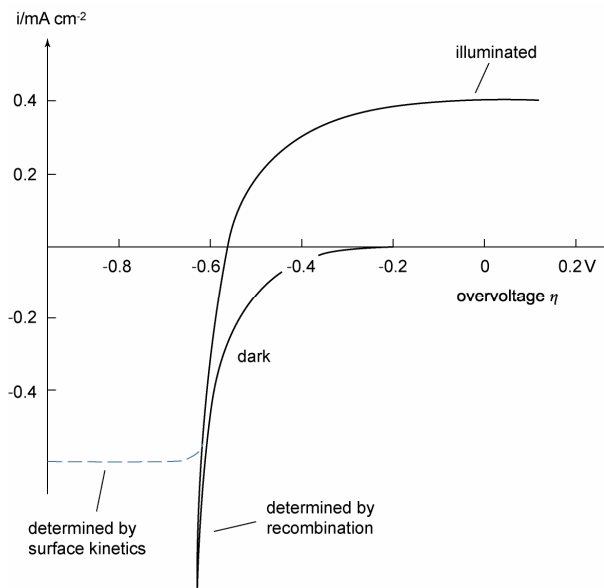


Figure 2.19 Theoretical current–potential curve for an *n*-type semiconductor in contact with a redox system, assuming a valence-band process.

meet the theoretical requirements; values much larger than 60 mV per decade have frequently been found. Even for materials that have a rather perfect surface because of their layered structures (*e.g.* WSe_2 , MoS_2), the current–potential dependence exhibits slopes greater than 60 mV. These deviations from theory are still not sufficiently understood. In the case of aqueous solutions, there are only two systems known where a 60 mV slope was found, namely the reduction of several redox systems at *n*-ZnO (Morrison, 1962) and the reduction of protons at *n*-GaAs (Uhlendorf *et al.*, 1995). Several investigations have shown later that with non-aqueous solutions, the proper slope is usually obtained when plotting $\log i$ vs. ϕ_{scI} .

Both theoretical (Lewis, 1991; Smith *et al.*, 1996; Smith and Nozik, 1996, 1997; Royea *et al.*, 1997) and experimental (Kasinski *et al.*, 1989; Lewis, 1990; Forbes and Rosenwaks *et al.*, 1992; Gomez-Jahn and Miller, 1992; Uhlendorf *et al.*, 1995, 1996; Fajardo and Lewis, 1996; Pomykal and Lewis, 1997; Meier *et al.*, 1997; Meier *et al.*, 1997, 1999) investigations have been conducted to determine the absolute values of rate constants for electron transfer across semiconductor–liquid interfaces. Lewis (1991) extended models introduced by Marcus and by Levich (Royea *et al.*, 1997), and estimated the maximum possible value of the second order rate constant ($k_{\text{c,max}}^+$, $k_{\text{c,max}}^-$) for outer-sphere redox acceptors to be 10^{-16} – 10^{-17} $\text{cm}^4 \text{s}^{-1}$.

Other authors (Smith and Nozik, 1996) have shown that the latter model leads to maximum values being 2–3 orders of magnitude higher. However, the validity of describing electron transfer across semiconductor–liquid interfaces in terms of classical electronic particles has been challenged, and quantum mechanical models based on the interaction of the full electronic structure of the semiconductor with that of the redox species in solution have been published (Smith *et al.*, 1996; Smith and Nozik, 1997). Adsorption effects have complicated experimental studies. Notwithstanding this, there are important conceptual differences in the formulation of the heterogeneous rate constant that merit further consideration. Further details concerning the coupling between electrode and electron acceptor or donor molecule in solution are given in Section 2.3.5.

At present, several experimental rate constant data are available, mainly obtained with different metallocenes as redox couples in CH₃OH or CH₃CN and *n*-type semiconductors such as Si, InP (Fajardo and Lewis, 1996; Pomykal and Lewis, 1997), GaAs and GaAsP₂ (Rosenwaks *et al.*, 1992; Meier *et al.*, 1997, 1999). In the cases of the reduction of FeCp₂⁺ (ferrocene derivatives) at *n*-Si and *n*-InP, maximum rate constants in the order of $k_{c,\max}^+ = 10^{-17}$ – 10^{-16} cm⁴ s⁻¹ were evaluated from the corresponding current–potential curves whereas for the reduction of CoCp₂⁺ (cobaltocene) at *n*-GaAsP₂ $k_{c,\max}^+ \approx 5 \times 10^{-16}$ cm⁴ s⁻¹ was obtained. In all these cases the cathodic current increased linearly with increasing concentrations of the redox system. Concerning the reduction of CoCp₂, much higher cathodic currents were observed with *n*-GaAs electrodes. Above a certain concentration the current became independent from the concentration. In this case, adsorption of the redox system has been found and according to the evaluation of the current–potential curve and of the corresponding impedance spectra, the $\log i_c$ vs ϕ_{sc} plot could be described by the thermionic emission model (Fig. 2.20) (Meier *et al.*, 1997, 1999). The theoretical current–potential curve based on the thermionic emission model is given by

$$i_{\text{therm}} = A_R T^2 \frac{m^*}{m_e} \exp\left(\frac{-q\phi_{sc}}{kT}\right) \exp\left(-\frac{E_c - E_F}{kT}\right) \quad (2.41)$$

with the Richardson constant $A_R = 120$ A cm⁻². According to this result, the rate of electron transfer must be very large so that the transport of electrons through the space-charge region becomes rate determining. An estimate of the corresponding rate constant yielded a value much larger than 10^{-14} cm⁴ s⁻¹.

Similar results have been obtained for the reduction of protons at *n*-GaAs electrodes. The thermionic emission process again limits the current (Uhlendorf *et al.*,

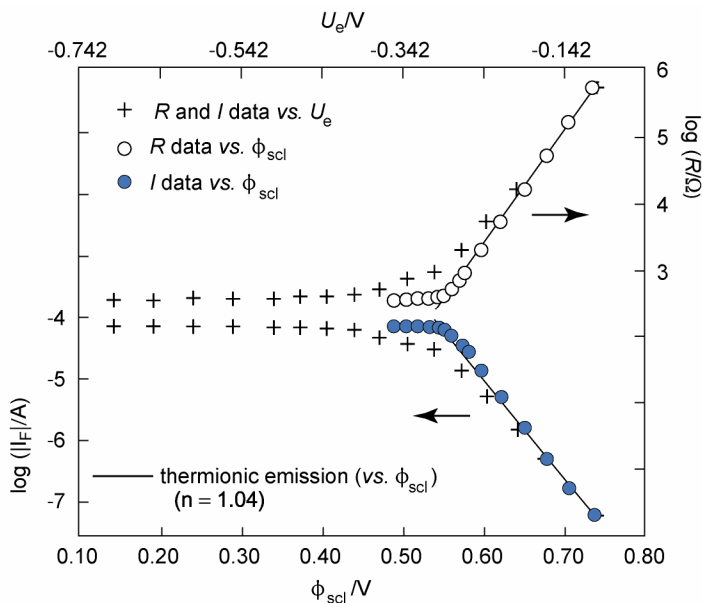


Figure 2.20 Reduction current vs. potential ϕ_{scl} across the space-charge region at n -GaAs in acetonitrile with cobaltocenium (CoCp_2^+); R = charge-transfer resistance, U_e = electrode potential (Meier *et al.*, 1999).

1995). As will be shown in Section 2.4, these observations have a large impetus on the performance of photoelectrochemical solar cells. It should also be mentioned the reverse processes, here the oxidation of the redox system, does not necessarily also occur via the conduction band. Since the reorganisation energies are typically in the range of $\lambda = 0.5\text{--}1.2$ eV, the oxidation of the redox couple may occur via the valence band, especially for semiconductors of a bandgap smaller than 2 eV.

2.4.3 Minority-carrier processes

The current equations, eqs. 2.36, 2.38 and 2.39, can also be written in such a way that the equilibrium conditions are taken into account. Setting $i_c^+ = i_c^- = i_c^o$ and $n_s = n_s^o$ at equilibrium and using eq. 2.36, the total current corresponding to an electron transfer via the conduction band can be written as

$$i_c = -i_c^o \left[\frac{n_s}{n_s^o} - 1 \right] \quad (2.42)$$

where

$$i_c^o = qk_c^+ N_c c_{\text{red}} \quad (2.43)$$

A similar expression can be derived for charge transfer via the valence band:

$$i_v = i_v^o \left[\frac{p_s}{p_s^o} - 1 \right] \quad (2.44)$$

in which p_s^o is the surface hole density at equilibrium and

$$i_v^o = qk_v^- N_v c_{\text{ox}} \quad (2.45)$$

To obtain relations between carrier density at the interface and at the inner edge of the depletion layer (the width w of the space-charge layer is defined by $w = \epsilon \epsilon_o / C_{\text{scl}}$), we assume a Boltzmann equilibrium for the carriers across the space-charge layer. We have then

$$n_s = n_w \exp\left(-\frac{q\phi_{\text{scl}}}{kT}\right) \quad (2.46a)$$

$$p_s = p_w \exp\left(\frac{q\phi_{\text{scl}}}{kT}\right) \quad (2.46b)$$

where n_w and p_w are the carrier densities at the inner edge of the space-charge region; these are not identical to the bulk densities n_o and p_o if minority carriers are involved in the reaction.

The carrier densities depend not only on the doping but also on the generation of charge carriers by light excitation. Minority carriers, generated by light excitation in the bulk ($x > w$), can only diffuse towards the surface, whereas those that are generated within the space-charge region are driven towards the interface by the electric field, as discussed in Section 2.2. In the case of an n -type semiconductor and following Reichman's derivation (Reichmann, 1980), the current generated in the space-charge layer is given by

$$i_{\text{scl}} = qj_o [1 - \exp(-\alpha w)] \quad (2.47)$$

where j_o is the incident photon flux density and α the absorption coefficient. The diffusion current, due to generation of holes in the bulk, can be obtained by solving the corresponding diffusion equation, and is given by

$$i_{\text{diff}} = -i_o \left[\frac{p_w}{p_o} - 1 \right] + \frac{qj_o \alpha L_p}{1 + \alpha L_p} \exp(-\alpha w) \quad (2.48)$$

with

$$i_o = \frac{qn_i^2 D_h}{N_D L_h} \quad (2.49)$$

where N_D is the donor density and D_h and L_h are the diffusion constant and diffusion length of holes, respectively. The two components of the hole current must be equal to the total current as given by eq. 2.44, *i.e.*

$$i_{\text{scl}} + i_{\text{diff}} = i_v \quad (2.50)$$

Inserting eqs. 2.44, 2.47 and 2.48 into eq. 2.50, we find

$$i_v = \frac{i_g - i_o \exp\left(-\frac{q\eta}{kT}\right)}{1 + \left(\frac{i_o}{i_v^o}\right) \exp\left(-\frac{q\eta}{kT}\right)} \quad (2.51)$$

in which η is the overvoltage with respect to equilibrium, *i.e.*

$$\eta = U_E - U_{\text{redox}} \quad (2.52)$$

and the generation current is given by

$$i_g = i_o + qI_o \left[1 - \frac{\exp(-\alpha w)}{1 + \alpha L_h} \right] \quad (2.53)$$

The second term in eq. 2.53 is actually the photocurrent, so that

$$i_g = i_o + i_{\text{ph}} \quad (2.54)$$

Equation 2.53 was previously derived by Gärtner (1959) for the photocurrent across a semiconductor/metal junction under reverse bias assuming $p_w = 0$. In the Reichman's derivation, however, p_w was obtained in a manner consistent with the interface boundary conditions, which include the hole-transfer kinetics. Therefore Reichman's derivation is much more general than that of Gärtner.

Equation 2.31 describes the complete current–potential behaviour for a pure valence-band process at an n -type electrode in the dark and under illumination. In the dark ($i_g = 0$), one obtains from eq. 2.51

$$i_v(\text{dark}) = \frac{i_o \left[\exp\left(-\frac{q\eta}{kT}\right) - 1 \right]}{1 + \left(\frac{i_o}{i_v^o}\right) \exp\left(-\frac{q\eta}{kT}\right)} \quad (2.55)$$

Using eqs. 2.51 and 2.55, current–voltage curves can be calculated as displayed qualitatively in Fig. 2.19 for a pure valence-band process at an n -electrode. At anodic polarisation (positive η values), the dark current will become $i_v(\text{dark}) \rightarrow i_o$, and the total current under illumination $i_v \rightarrow i_g$. The cathodic current–potential behaviour depends on the ratio of i_o/i_v^o . Referring to eqs. 2.45 and 2.49, these two currents represent the generation/recombination rate of the minority carriers in the bulk of the semiconductor (i_o) and the rate of hole injection at the interface (i_v^o). The first current depends entirely on the properties of the semiconductor, whereas i_v^o is mainly controlled by the energetic conditions at the interface and the concentration of the redox system. Accordingly, the ratio i_o/i_v^o actually controls whether the generation/recombination process or the surface kinetics are rate-determining. Assuming the hole injection is relatively slow ($i_v^o \ll i_o$), for large negative η values eq. 2.55 gives

$$i_v(\text{dark}) \rightarrow -i_v^o \quad (2.56)$$

as indicated by the dashed curve in Fig. 2.19. This kinetically-controlled current should increase linearly with c_{ox} . On the other hand, if the recombination controls the current ($i_v^o \gg i_o$), then one obtains

$$i_v = -i_o \left[\exp\left(-\frac{q\eta}{kT}\right) - 1 \right] + i_{\text{ph}} \quad (2.57)$$

As we noted before, this equation is valid for a pure valence-band process. This has only been found experimentally for redox systems where the standard potential occurs very close to the valence band ($E_{\text{F,redox}} - E_v \leq 0.2$ eV) as proven, for instance, for the reduction and oxidation of $\text{Cu}^{1+}/\text{Cu}^{2+}$ system at GaAs electrodes in aqueous solutions (Reineke and Memming, 1992). In other cases where the standard potential of the redox system occurs closer to the middle of the bandgap so that the reduction of a redox system is expected to occur via the conduction band. Using eq. 2.42 we have then

$$i = -i_c^o \left[\exp\left(-\frac{q\eta}{kT}\right) - 1 \right] + i_{\text{ph}} \quad (2.58)$$

This is the same type of $i - \eta$ relation as given by eq. 2.57; the two differ only by the pre-exponential factor. Experimentally, it is often not easy to distinguish between these two processes. One way of doing so is to measure the $i - \eta$ curve with a p -type

electrode of the same material. If the cathodic dark current is really large, *e.g.* diffusion-limited, then it must be a valence-band process because only in this band are there sufficient electrons available in *p*-material. If only *n*-type electrodes are available, one can use materials of different doping, which would lead to different i_0 values (eq. 2.49).

2.4.4 The quasi-Fermi level concept for electron-transfer processes

When applying an external voltage to a semiconductor electrode, it occurs as the difference between the electrochemical potential in the solution (Fermi level of the redox system) and the Fermi level in the semiconductor electrode, as illustrated for an *n*-type semiconductor in Fig. 2.16. Being more precise, the latter is the Fermi level of the majority-carriers. It is also sufficient to consider only this Fermi level if majority-carriers are transferred across the interface. The difference of the Fermi levels on both sides of the interface is, thermodynamically speaking, the driving force for the corresponding reaction. If no other reaction occurs, then the minority carriers are still in equilibrium with the majority-carriers; that is, the quasi-Fermi levels of holes and electrons remain equal ($E_{F,n} = E_{F,p}$) even during current flow. The Fermi level is constant within the solid, including the space-charge region, as proved by measurements of the space-charge capacitance (Mott–Schottky plot).

The situation is quite different if minority carriers are involved. Then electrons and holes are not in equilibrium and their quasi-Fermi levels become different. In the case of an *n*-type semiconductor, $E_{F,p}$ can be located above or below $E_{F,n}$, depending on the minority-carrier process; *i.e.* whether minority carriers are extracted from or injected into the semiconductor. Reactions at *n*- and *p*-type electrodes can be analysed quantitatively in terms of quasi-Fermi levels (Reineke and Memming, part 1, 1992).

In the present derivation we take a valence-band process as an example. According to the quasi-Fermi level concept, it is assumed that the same reaction with identical rates, *i.e.* equal currents, takes place at *n*- and *p*-type semiconductor electrodes of the same material if the density p_s of holes at the surface—or equivalently the quasi-Fermi levels $E_{F,p}$ —are equal at the surface of the two types of electrodes, as illustrated for an illuminated *n*-electrode and a *p*-electrode in the dark in Fig 2.21. This model is applicable if three conditions are fulfilled:

1. At equilibrium, the conduction and valence band edges at the surface of the *n*- and *p*-type electrode have the same position.
2. All electrode reactions can be described as a function of the surface hole density.

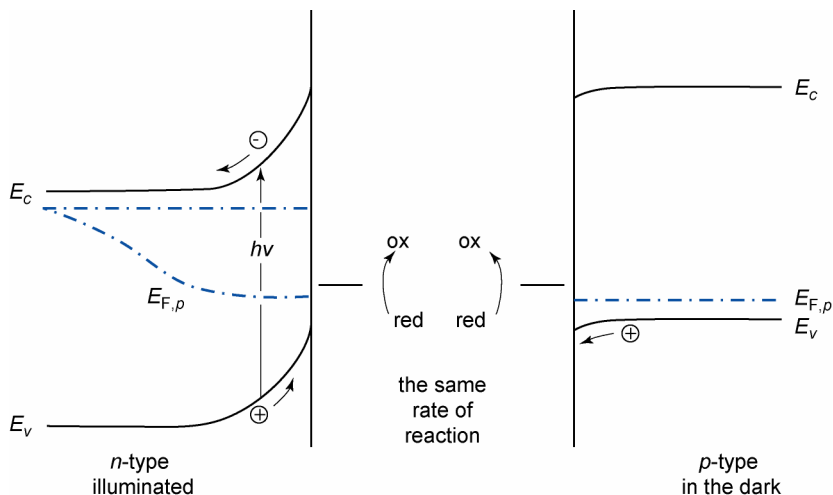


Figure 2.21 Principle of comparability of reactions at *n*-type and *p*-type electrodes.

3. The holes at the surface of the *p*-type electrode are nearly in equilibrium with those in the bulk, *i.e.* the Fermi level of the majority carriers is constant within the electrode.

Equivalent conditions can be expressed for a conduction band process. In this case electrons are the majority-carriers. This model has experimentally been proved by studying the $\text{Cu}^{1+/2+}$ redox reaction and the anodic decomposition process at GaAs electrodes (Meissner and Memming, 1992; Reineke and Memming, 1992).

The advantage of the model presented here is as follows: the quasi-Fermi level of the majority carriers can be determined because it is identical to the electrode potential. Since the current–potential curve measured with the *p*-GaAs electrode yields directly the relation between $E_{\text{F},p}^s$ and the hole current (dark current at *p*-GaAs), the position of the quasi-Fermi level of holes (minority carriers) at the surface of the *n*-type electrode is then also known for a given current (dark or photocurrent). This is illustrated in Fig. 2.22. The saturated anodic photocurrent at the *n*-electrode has a value of $i_{\text{ph}} = 0.44 \text{ mA cm}^{-2}$. The same current at the *p*-electrode occurs at $U_{\text{F}} = 0.28 \text{ V}$, *i.e.* the quasi-Fermi level of holes occurs for both types of electrodes at $E_{\text{F},p}^s = +0.28 \text{ eV}$.

It should be noted that an anodic current (valence-band process) at the *p*-type electrode, as well as at the corresponding *n*-type electrode, occurs only if $E_{\text{F},p}^s$ is located below the redox potential, as illustrated in Fig. 2.21. This is a necessary

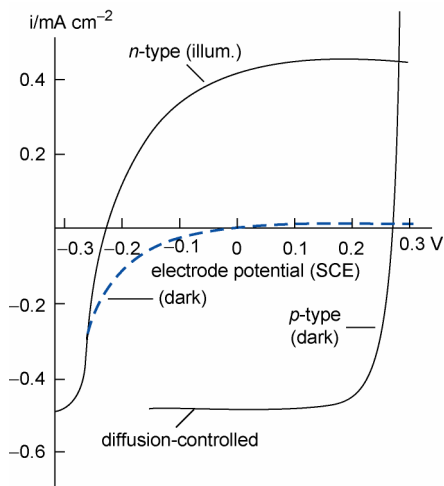


Figure 2.22 Current-potential curves for *n*- and *p*-type GaAs in 6 M HCl with $\text{Cu}^{2+}/\text{Cu}^{+}$ as a redox system (Reineke *et al.*, 1992).

condition both in the dark and during light excitation. Polarising an *n*-type electrode anodically usually causes a very small, but constant, anodic current to be observed in the dark. Such a small current occurs at $U_F = 0.26$ V for the *p*-electrode, *i.e.* $E_{F,p}^s = +0.26$ eV (Fig. 2.22). Any further polarisation leads to a larger band bending and to a downward movement of the quasi-Fermi level of electron (majority carriers). The quasi-Fermi level of holes, however, remains at the same position (very slightly below the redox potential), because the current remains constant.

Some authors have asserted that the quasi-Fermi level model requires a threshold with respect to light intensity. This problem has been discussed for photoconversion systems such as photoelectrolysis of H_2O (Gregg and Nozik, 1993; Shreve and Lewis, 1995). Since the discussion on the threshold problem has frequently led to misinterpretations, we want to clarify the situation by considering a simple charge-transfer between an *n*-type semiconductor and redox system, as illustrated in Fig. 2.23. The system is at equilibrium ($i = 0$) if the overvoltage is zero ($\eta = 0$). Here the quasi-Fermi levels of electrons and holes are both equal to $E_{F,\text{redox}}$ (not shown). Assuming that the redox process occurs entirely via the valence band, then only the quasi-Fermi level of holes at the surface, $E_{F,p}^s$, is of interest. Anodic polarisation of the electrode in the dark produces a very small anodic current (lower i - η curve in the centre of Fig. 2.23). As mentioned in the previous section, $E_{F,p}^s$ is practically pinned close to $E_{F,\text{redox}}$ (Fig. 2.23A) whereas $E_{F,n}$ differs from $E_{F,\text{redox}}$ by $q\eta$. On illumination, the anodic

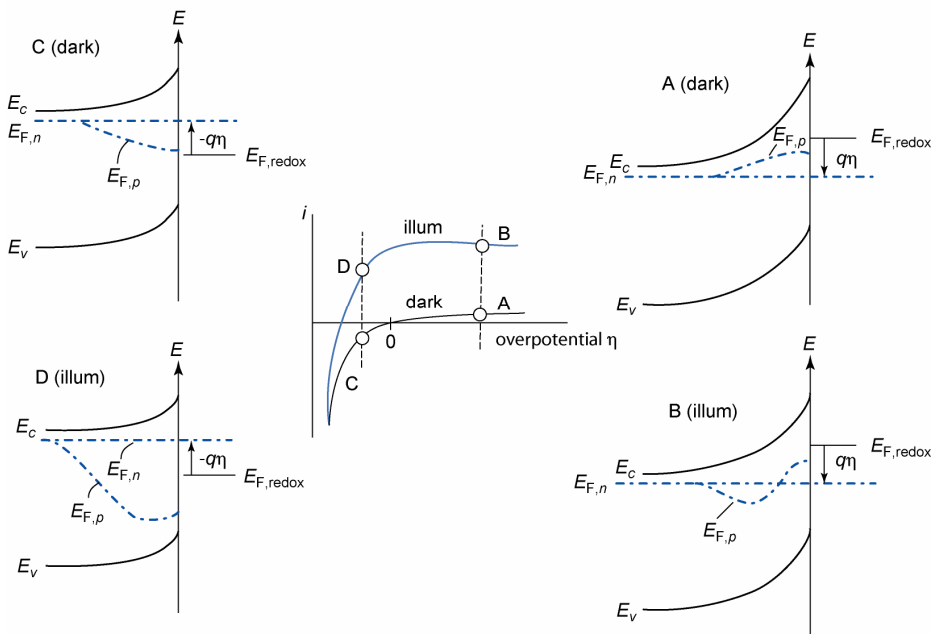


Figure 2.23 Positions of quasi-Fermi levels at high positive overpotential (A and B) and low negative overpotential (C and D) in the dark and under illumination; centre: current–potential curve for an n -type semiconductor electrode (Memming, 2000).

current increases and $E_{F,p}^s$ is shifted downward whereas $E_{F,n}$ remains unchanged (Fig. 2.23B). The shift is small at low light intensities and large at high intensities. Since the dark position of $E_{F,p}^s$ occurs already below $E_{F,redox}$, there is no threshold for the anodic photocurrent with respect to light intensity. Under cathodic bias, $E_{F,p}^s$ lies above $E_{F,redox}$ because of the cathodic dark current (Fig. 2.23C). Here the difference between $E_{F,n}$ and $E_{F,p}^s$ is of interest insofar as it determines the recombination current. Under illumination, an anodic current flows as shown by the i - η curve. In this case, $E_{F,p}^s$ moves below $E_{F,redox}$ if the total current becomes positive (Fig. 2.23D). Accordingly, at low intensities i_{tot} remains negative; *i.e.* the hole injection still dominates. This is, however, not a real threshold. It must be remembered that the difference between $E_{F,p}^s$ and $E_{F,redox}$ is the driving force of the reaction and the relative position of the two Fermi levels determines the direction of hole transfer. The same type of argument is applicable when describing the photoelectrolysis of H_2O in terms of the quasi-Fermi level concept.

2.4.5 Interfacial charge-transfer dynamics

The above discussion of energetics and primary photophysical processes lay the ground work for understanding photoinduced electron-transfer processes at semiconductor interfaces. The electron-transfer step is the primary event responsible energy transduction. For this reason, a number of detailed reviews of the various aspects of the electron-transfer process are given throughout this volume. This section will focus on the dynamics of the electron-transfer process. Relative to other photophysical processes, information on the electron-transfer dynamics provides a microscopic description of the overall energy conversion process and can be related to fundamental parameters that are amenable to optimisation. The picture that is conveyed in this section will hopefully provide a unifying conceptual basis for understanding the reviews of the diverse phenomena that in the following chapters.

The electron-transfer step involves the mixing of electronic states defined by the periodic lattice of a solid-state system and a molecular system—modulated by the nuclear dynamics of the bath. The starting basis set for describing this electronic mixing is the unperturbed eigenstates of the solid-state and the molecular state. As discussed in Section 2.2, the energy levels of the solid-state are sufficiently close together ($\Delta E \ll kT$) that they constitute an electronic continuum. This large density of electronic levels has interesting consequences for treating the electron-transfer coordinate. First, the solid-state wavefunctions are highly delocalised. Relative to the spatial charge distribution within the solid-state half-space of the interface, the molecular state appears as a pinhole in the total available electronic phase space available to the charge carrier in the crystal. In order to localise the charge on the molecular acceptor, the nuclear fluctuations along the reaction coordinate (medium repolarisation) must lead to sufficient stabilisation of the charge on the molecular state to lower the electronic level of the acceptor below that of the band extrema. At each barrier-crossing event, the charge carrier is able to scatter into other $\mathbf{k}$ and $\mathbf{r}$ space positions until the electronic surface of the mixed states relaxes below that of the band states. Thus, the electronic continuum acts to reduce the transmission probability for localisation of the reactive charge carrier on any particular molecular state. This aspect of the problem is unique to photoinduced charge-transfer processes at conducting surfaces in which the absorption of light creates carriers in the solid-state far from thermal equilibrium. Under these conditions, the carriers are optically created in a sea of electronic states that are unoccupied and compete with any molecular acceptor state (electron or hole) for the charge density. In this regard, the space-charge field plays a critical role not only in spatially confining the minority photocarriers to be within good spatial overlap but also in reducing the non-reactive

electronic phase space available for scattering the carrier away from the reaction saddle point. Essentially, the space-charge field decreases the effective volume of the crystal available to the reaction coordinate.

To make the effect of the electronic continuum on the reaction dynamics as transparent as possible, consider the discrete two-state coupling problem representative of homogeneous electron transfer. In this problem, an electron is transferred between two localised molecular states. The electron-transfer rate constant (k_{ET}) is given by the well-known expression (Marcus and Sutin, 1985)

$$k_{\text{ET}} = \nu_{\text{eff}} \kappa(r) \exp \left[\frac{-(E - E_{\text{redox}} - \lambda)^2}{4\lambda kT} \right]; \kappa(r) = e^{-\beta r} \quad (2.59)$$

where ν_{eff} is the effective rate of nuclear passage through the reaction saddle point, and $\kappa(r)$ defines the distance-dependent electronic coupling. The electronic coupling decays exponentially with distance with a damping constant β that reflects the decrease in wavefunction overlap. The exponential term, depending on the reorganisation energy λ , gives the nuclear activation barrier. This latter term was derived assuming thermally averaged Franck–Condon factors and a harmonic approximation to the bath coordinate (linear dielectric response). The nuclear potential energy coordinate is shown in Fig. 2.24 for a self-exchange reaction. The most salient feature is the barrier crossing point (B in Fig. 2.24). At this point in nuclear configuration space, the donor and acceptor electronic states are resonant. The two states mix to develop an avoided crossing that splits the reactant and product surfaces by $2V_{12}$. The overall rate of passage depends on both the electronic and nuclear coordinate at this point. If the two states are spatially far apart, the electronic mixing is weak ($2V_{12} \ll kT$). This is the *slow electron case*. If one could freeze the nuclear coordinate with the electron localised on the donor, the electron probability would oscillate back and forth between the donor and acceptor at the tunnelling period. For weak-coupling conditions, this change in electron probability is much slower than the nuclear fluctuations, so that only a very small amount of electron probability leaks over to the donor state ($\kappa(r) \ll 1$) before nuclear motions drive the two states apart energetically. Under this condition, the system moves primarily along the reactant surface and only infrequently samples the product surface. This is the weak coupling or nonadiabatic limit where the equilibration of the electronic coordinate is much slower than the nuclear fluctuation time scale. As one brings the molecules closer and closer together, the wavefunction overlap increases and the electron tunnelling time within this frozen coordinate would decrease. At some point, the electron probability

would oscillate between the two states faster than the nuclear fluctuations. This would be the *fast electron case*. Under this condition, the electronic coordinate stays equilibrated with the nuclear coordinate and adiabatically follows the nuclear coordinate from the reactant to the product surface ($\kappa(r) = 1$ in eq. 2.59).

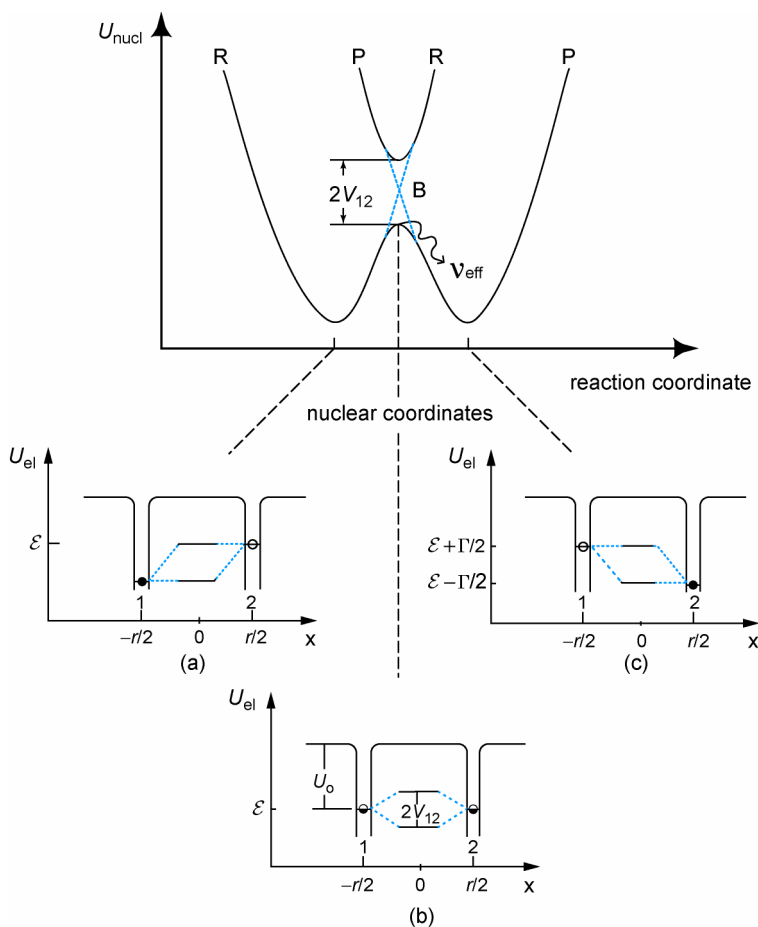


Figure 2.24 Potential energy diagram for homogeneous electron-transfer self-exchange. The top curve is a one-dimensional slice through a complex multi-dimensional potential energy surface U in which the nuclear motions are assumed to be within harmonic limits. The corresponding electronic diagrams are shown below: (a) system configuration favours electron localisation on the donor; (b) at the reaction saddle point the donor and acceptor levels become resonant; and (c) the nuclear configurational repolarisation creates a local environment where the electron energy is lower on the acceptor. Based on Sutin and Marcus (1985).

The key point of the above discussion is that fundamentally the electron-transfer rate constant is limited by the dynamics of the nuclear motion across the reaction saddle point. Any nuclear activation barrier reduces the magnitude of the electron-transfer rate constant from this fundamental upper limit. In other words, *electron transfer cannot occur faster than the nuclear motions that lead to localisation on the molecular acceptor* that is defined to be the product state in this discussion. If the dominant portion of the medium repolarisation energy arises from relaxation of the solvent along the electron-transfer coordinate, this time scale is determined primarily by the solvent motion. In cases where there is significant intramolecular reorganisation energy, the intramolecular coordinate may play the deciding role. In either case, this motion is not instantaneous. The solvent reaction/relaxation to the reaction field is related to its dielectric relaxation response. The time course of this relaxation is not a strictly exponential response that would ordinarily belie a continuous stochastic process. Rather, there are non-diffusive relaxation components determined by inertial motions (free streaming motion in the absence of inelastic collisions with other modes/nuclei) followed by slower diffusive translational and reorientation motions of the solvent molecules. The inertial motions can be understood if one considers the displacement of the motions prior to collisions in the presence of the reaction forces. Those motions that locally lower the energy of the system experience a much larger displacement than motions opposing the reaction force. For most polar liquids, at least half the energy of reorganisation is carried by these inertial motions that occur on 10 to 100 fs time scales (comparable with electron–phonon scattering times but with substantially larger electron–phonon coupling constants). The diffusive relaxation components occur over distributed time scales that depend on the repolarisation volume, viscoelastic effects, and degree of association. The specific details of the solvent coordinate have been reviewed and there is now a fairly extensive compilation of the various solvent response functions for most liquids (Maroncelli, 1993). Given the complex solvent response, it is difficult to use typical notions of a constant to define adiabatic limits. However, to a first-order approximation, the effective relaxation time (ν_{eff}^{-1}) can be approximated by the longitudinal dielectric relaxation time of the liquid. This time constant is the high-frequency response of the liquid to an applied electric field. In the electron-transfer case, the relevant electric field is the change in dipolar field that arises from the charge displacement associated with electron transfer. In almost all cases, the solvent coordinate determines the dynamics for electron transfer. Outer-sphere reorganisation energies are typically of around 1 eV, whereas inner-sphere, intramolecular, reorganisation energies are typically about 0.3 eV or less (Marcus, 1985). The intramolecular repolarisation of the various modes coupled to the reaction coordinate occurs on the same time scale as intra-

molecular vibrational energy redistribution. The distortion of a mode in response to the change in charge involves coupling of the unperturbed basis of vibrational states and is thus virtually identical to intramolecular vibrational redistribution processes. These dynamics have been extensively treated in the context of vibrational energy relaxation and have similar dynamics to the inertial components of liquids. The intramolecular coordinate has not been shown to be a dominant factor and from here on it will be assumed that the solvent coordinate demarcates adiabatic behaviour.

In contrast to the above two state description, the solid-state electronic levels represent an N -level problem; where N is a very large number. The non-equilibrium charge distribution created by light absorption will relax into all available degenerate and lower energy electronic levels. Molecular acceptors at the interface represent only one possible electronic channel among the multitude of available states. Most of the electronic states in the solid state will contribute to a time-dependent wavefunction for the charge density that reduces the density at the surface, so the surface atoms and molecular state are only a small fraction of the total number of mixed states. Again, the net effect of the large electronic density is to reduce the transmission probability at the reaction saddle point for any particular molecular state.⁷

Figure 2.25 shows the effect of the large manifold of electronic states graphically. The upper figure shows the two-state coupling problem within a frozen nuclear coordinate description. The electron density is initially localised at the donor site and oscillates back and forth with 100% modulation at the tunnelling period. As the number of coupled sites increases, the occurrence time increases and the fractional probability at the initial site decreases. To highlight this point, the lower figure shows a calculation in which the electron is initially localised one atomic lattice plane below the surface from this same acceptor within a lattice of 27 atoms that represent the crystal lattice. Here, it is obvious that the oscillations in charge density at the molecular acceptor site are significantly smaller than in the two-state case, owing to the presence of the additional electronically-resonant atoms available for electron exchange. In addition, the charge-density fluctuations appear to become chaotic due to the numerous constructive and destructive pathways for the electronic wavefunction.

⁷ The reduced transmission probability at a single site should scale as the ratio of the scattering rate to the non-reactive $\mathbf{k}$ and $\mathbf{r}$ states to the rate of barrier crossing. For example if the phonon-scattering rate is 10^{13} s^{-1} within the solid-state and the effective solvent relaxation rate is 10^{12} s^{-1} , the transmission probability would be attenuated by an order of magnitude. There are however two compensating features. The larger effective electron-phonon coupling to polar fluid motions increases the transmission probability to the molecular site and the fast carrier transport leads to larger sampling of surface acceptors and increased transfer rate.

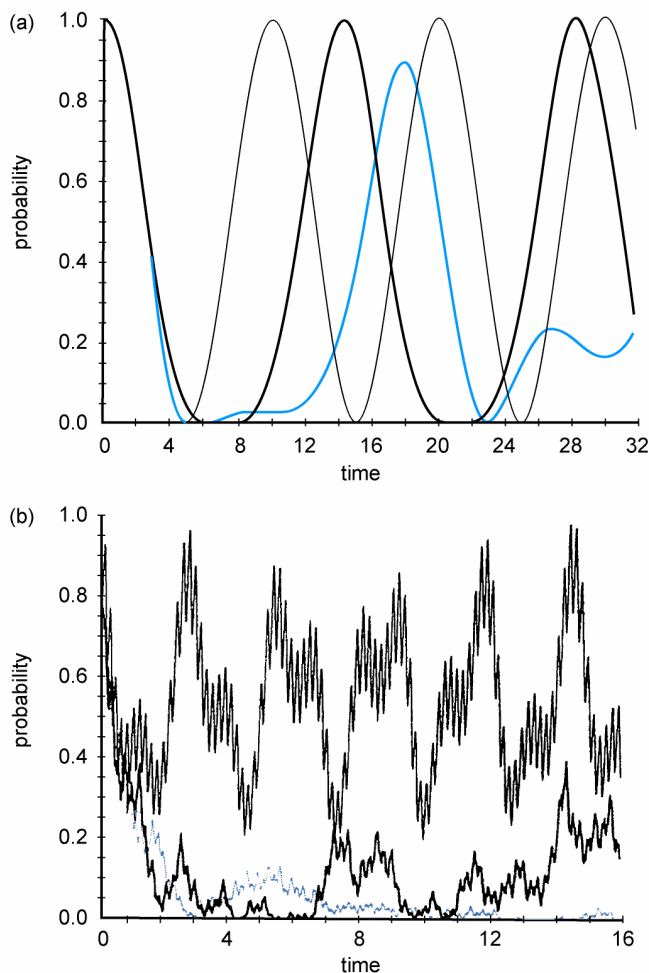


Figure 2.25 Effect of N level coupling. (a) Electron probability residing at the initial (donor) site for 2 (thin black line), 3 (heavy black line) and 4 (continuous blue line) sites coupled in a linear fashion. (b) Calculation repeated for a cubic lattice with 27 (thin black line); 343 atoms (thick line), and 512 atom clusters (blue line). The time base corresponds to periods of the lattice eigenvalues (Lanzafame *et al.*, 1994).

The only way the electron can be localised on this model acceptor site is if some perturbation makes it lower in energy than the resonantly coupled atomic sites of the lattice. This perturbation is the nuclear fluctuation of the dielectric medium that displace the nuclear configurations towards position C in Fig. 2.24 where the charge-

separated state is more stable.⁸ *In all cases, the lower limit to the electron-transfer time scale to a molecular acceptor is fundamentally determined by the nuclear motion through the reaction saddle point.* Atoms must move to produce a net repolarisation of the medium that stabilises the charge-separated product channel.

It is important to emphasise that the above arguments have so far been based on barrierless processes. Any nuclear activation barrier to charger transfer will retard the time evolution from the reactant to the product surface. This discussion also assumes adiabatic coupling conditions. The reason for taking this starting position is that these conditions define the fastest possible times for electron transfer. Relative to other competing channels, the above conditions also define the maximum efficiency. Any other process decreases either the quantum yield for charge separation or involves inelastic or heat dissipation processes that equate to energy conversion losses. Barrierless conditions, within adiabatic coupling limits, were considered to be an unachievable set of conditions for many years. Virtually all the work in the electrochemical community pointed to exclusive weak-coupling conditions for the electronic coupling. There was in fact only one published report in the mid-1980s that gave experimental evidence for the possibility of adiabatic coupling conditions (Iwasita *et al.*, 1985). Since this work, there have been significant advances in the application of real-time spectroscopies to follow the dynamics of charge transfer at semiconductor surfaces.

Figure 2.26 shows representative data depicting hole transfer at GaAs(100)/Se^{2-/1-} aqueous liquid contacts. This liquid contact was the first to show very high quantum yields for photocurrent and solar energy conversion efficiencies comparable to the best solid-state junctions at the time. The hole transfer dynamics were determined using a holographic grating method to watch the wavefunction collapse onto the molecular state (Wang *et al.*, 1995). The most important finding is that hole transfer occurs within 1–2 ps. This time scale is essentially identical to the longitudinal relaxation time of water under the high ion concentrations present at the electrode double layer. This finding illustrated that the secret to the success of the GaAs aqueous contact is that it is kinetically stabilised in the presence of high concentrations of Se²⁻ hole scavengers. The other processes of surface-state trapping and photocorrosion are much slower. Basically, faster is better. The faster the electron-transfer step, the larger the difference in respective quantum yields between the desired energy-storing charge transfer step and the competing, deleterious, side

⁸ Should the charge carrier become trapped at a surface-state, then the problem becomes virtually identical to the homogenous two-state problem, *i.e.*, the donor and acceptor states are both spatially localised over dimensions comparable to typical molecular dimensions.

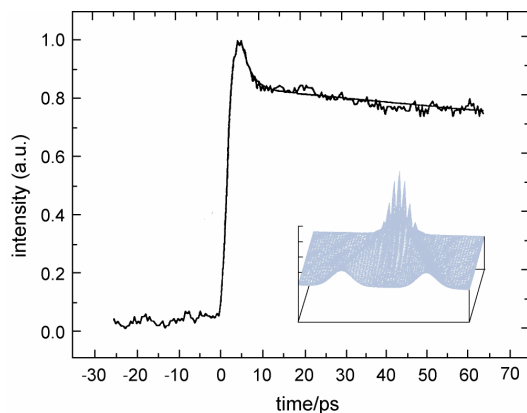


Figure 2.26 Time-resolved surface restricted transient grating studies of the n -GaAs(100)/Se^{2-/1-} aqueous liquid junction. The solid line through the data is the best fit to the data, yielding an initial 1 ps decay component that was assigned to interfacial hole transfer. This component depends on the Se²⁻ concentration and surface hole density (via bias dependence) and is approximately the signal magnitude based on the relative effective mass of the hole relative to that of the electron. The inset shows the optical pattern imaged into the surface by the photogeneration of free carriers and surface space-charge focussing of the minority carrier to the surface (Wang *et al.*, 1995).

processes. The GaAs(100)/Se^{2-/1-} aqueous liquid contact attests to the virtues of exploiting the dynamics of interfacial charge-transfer to fully optimise the surface photochemistry. Equally important, the observed dynamics at this interface demonstrate that it is possible, in fact, to have electron-transfer processes to molecular acceptors occur within adiabatic coupling limits. Since the electron-transfer time scale is fundamentally limited by the solvent dynamics, it is difficult to quantify the degree of electronic coupling from the above study. However, a lower limit can be established. Based on the observed dynamics, this work indicates that the electronic coupling between the spatially delocalised band states and molecular states at the surface is at least in the range of 10–100 cm⁻¹.

The acceptor in this study is the strongly physisorbed Se²⁻ and it could be argued that fast charge-transfer dynamics at this interface are not representative of the conditions required for efficient ion-current production. Recent studies of outer-sphere acceptors (ferricenium/ferrocene) using surface quantum well structures to avoid carrier transport and transient field effects on the dynamics have found evidence for electronic coupling parameters in the 100 cm⁻¹ range (Diol and Miller, 1998). Studies of anodic dark currents and acceptor concentration dependences of photocarrier lifetimes also find evidence for strong mixing between the molecular acceptors and the band states. Some of this is due to surface adsorption and will

require further study to quantify (Meier *et al.*, 1999). There is also evidence mounting from studies of the distance dependence for electron transfer using self-assembling monolayers on Au electrodes that the electronic coupling to classic outer-sphere (weakly physisorbed) acceptors in contact with the surface can have electronic coupling parameters on the order of 1000 cm^{-1} (Weber *et al.*, 1997; Diol and Miller, 1998). The most direct determination of the electronic coupling comes from measurements of the electron-transfer time for dye-sensitised systems. This body of work will be discussed in the next section. For the present discussion, it is clear from a number of studies of excited-state lifetimes at semiconductor surfaces that the magnitude of the electronic coupling for molecules in contact with a surface can be appreciable.

From the electronic coupling parameters and typical damping constants for the wavefunction overlap, it now appears that even molecules that are solvent-separated from the surface should experience electronic couplings as large as 100 cm^{-1} and be available for adiabatic electron-transfer processes with the appropriate energetics. This new understanding constitutes a significant departure from earlier work based on electrochemical studies alone. It should be emphasised that the electronic coupling between the surface and acceptor states can vary significantly in the range from 1000 cm^{-1} to 0 cm^{-1} depending on the surface structure and distance of the acceptors from the charge reservoir of states. Conditions such as surface contamination, surface roughness and solvation effects can all decrease the coupling from the adiabatic limit. The main point is that photoinduced charge-transfer processes from semiconductor electrodes to molecular states *can occur in the strong-coupling limit* rather than the generally assumed conditions of weak coupling. Since the mobile charge carrier must undergo spatial transport to a reactive site, this process is second order and the overall rate depends on the surface concentration of acceptors. As long as the concentration is high enough, the charge-transfer dynamics can approach picosecond and even femtosecond dynamics—as governed by the nuclear/solvent relaxation dynamics.

Charge-transfer dynamics on this time scale are competitive with carrier thermalisation processes (Section 2.2) so that it should be possible to engineer interfaces to minimise energy conversion losses through carrier relaxation processes in the solid-state. In retrospect, this statement could be considered obvious. Fundamentally, the carrier relaxation to either lower energy **k** states within the solid-state or charge-transfer products both involve, effectively, phonon-scattering mechanisms. In the solid-state, the spatially delocalised wavefunction is mixed with lower energy **k** states through a dense manifold of collective lattice vibrations (low carrier limit; negligible carrier–carrier scattering). In contrast, the relaxation of the charge carrier on to a molecular state involves much more localised molecular vibrations and solvent motions. The solvent fluctuations can only be construed to be collective or phonon-

like for very short time periods during which the motions are correlated. In either case, the mechanism is the same. The only difference is the degree of electron–phonon coupling. Because of the more localised nature of both the charge distribution and the effective phonon fields, the electron–phonon coupling (using the same nomenclature as Section 2.2) is nearly an order of magnitude larger in the liquid half-space of the reaction coordinate (for polar fluids) than within the solid-state.⁹ In this regard, the real advance in our thinking is the realisation that inertial contributions to the solvent relaxation, or scattering rate, could be comparable to phonon-scattering rates in the solid-state, and could occur on 100 fs time scales. Due to the much stronger modulation of the electron energy at the molecular site, if a charge carrier spatially samples a reactive crossing point, it is much more likely to collapse onto the molecular site than scatter to other **k** and **r** states in the solid. The key to optimally designing interfaces for energy conversion is to increase the collision frequency of the carriers with the reactive sites. This can be accomplished by increasing the surface concentration of acceptors, proper energetics for maximal overlap of the acceptor distribution with the donor levels of the solid-state, and by spatially confining the carriers (space-charge field or size/quantum confinement). Under optimal conditions, the interfacial charge-transfer dynamics can be competitive with all the other known photophysical processes acting on the non-equilibrium carrier distribution.

2.4.6 Dye sensitisation

Chapter 8 includes discussion of this field, so this section will be brief and will focus on the salient fundamental details relevant to this overview. Dye-sensitised surfaces have been extensively studied as a means to introduce colour sensitivity to photography. Efforts in the field of solar energy conversion have been directed to increasing the effective absorptivity of semiconductors to a larger fraction of the solar spectrum. Considerable effort was expended on wide band-gap semiconductors in this regard, but the more desirable electrochemical properties of large band-gap materials (resistance to photo-oxidation and corrosion) were offset by the extremely small fraction of the solar radiation absorbed by wide-band semiconductors. This earlier work and in-depth review of the relevant energetics for electron injection from dye-sensitised surfaces is given elsewhere (Memming, 1983).

⁹ The difference in reorganisation energy can be estimated from the static and optical dielectric properties of the liquid and solid-state (see Sutin and Marcus (1985) for liquid state and eq. 2.17 for the solid-state; $2\pi\nu_{\text{eff}} \approx \omega_{\text{op}}$).

The most important feature of this problem is the effect of the electronic continuum (conduction and valence bands) on the reaction coordinate (Lanzafame *et al.*, 1992; Miller *et al.*, 1995). Due to the large electronic bandwidth of the bands, it is much more feasible to construct a system in which optical excitation prepares the system for charge-transfer under barrierless conditions. This point pertains to dye excited-state levels that lie above the conduction-band minimum (in principle, this statement also pertains to ground-state hole levels that lie below the valence-band maximum for hole-transfer processes). For dye levels below the CBM, the conventional Levich–Marcus description is appropriate as the electron-transfer dynamics will be dominated by the activation barrier and be greatly retarded. In this latter case, even a small barrier ($\Delta E \approx 0.1$ eV) is sufficient to make the nonradiative electron-transfer process non-competitive with other radiative and nonradiative decay channels of the excited state. In this event, long-lived excited states reached by intersystem crossing to different spin manifolds are required to achieve reasonable quantum efficiencies. As a general rule, it is preferable to construct the system for barrierless electron transfer. Under barrierless conditions, the electron is initially localised on the dye. However, the electronic mixing of the dye's excited state with the band states produces a non-stationary state that is spatially unbounded. The electron is free to spatially propagate into the conduction band. Herein lies the key distinction of electron transfer involving dye-sensitised semiconductor surfaces. The electronic continuum of the band serves the same function as the nuclear continuum (see Section 2.3.5) in localising the electron in the product channel. In this case, the product state is defined as the electron being localised (>90%) within the solid-state half space of the reaction coordinate. The electron initially residing, spatially, on the dye is free to propagate into the solid-state as determined by the effective electronic coupling to the band states. Once the electron probability builds up an atom comprising the solid-state lattice, the recurrence time of the wavefunction on the original site becomes exceedingly long. The electron is much more likely to visit other lattice sites than the initial site. Before any significant electron probability can build back up on the initial site, an elastic or inelastic scattering event occurs in the solid state to dephase the coherently coupled states and localise the wavefunction in the solid state. This effect is shown by the quantum calculations depicted in Fig. 2.27.

The above concept was first realised from experimental studies of electron-transfer dynamics to dye-sensitised single crystal surfaces of SnS_2 (Lanzafame *et al.*, 1992; Lanzafame *et al.*, 1994). This semiconductor is one of the few systems that illustrate high (>80%) quantum yields for electron collection efficiencies. Only silver halides, nanocrystalline TiO_2 , and SnS_2 and other layered semiconductors exhibit high quantum efficiencies for photoanodic current production. Generally the yield is less

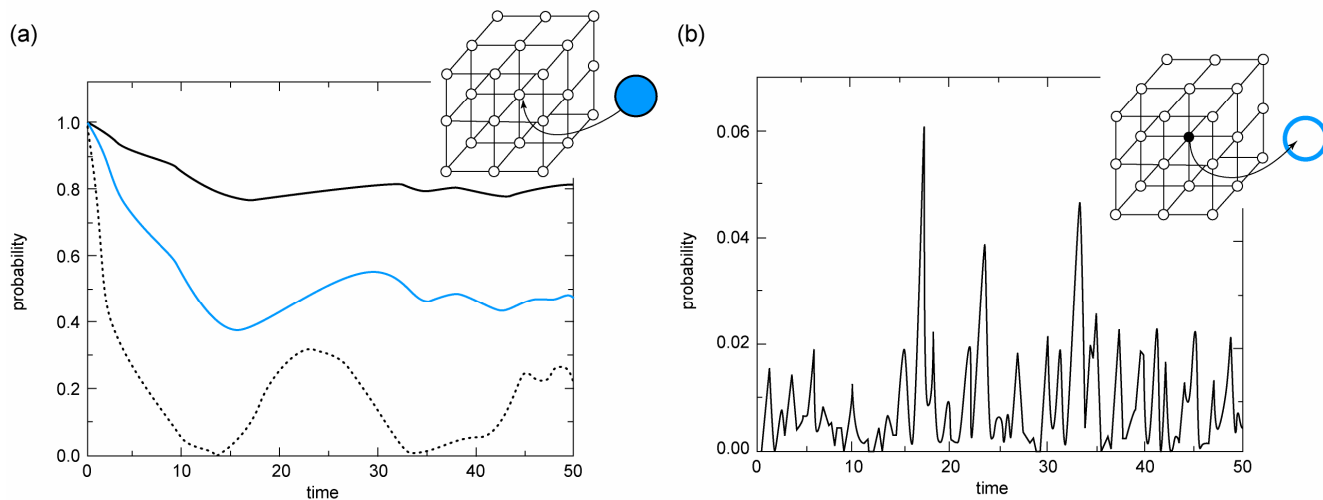


Figure 2.27 Model calculation. (a) Probability of the electron residing on the initial donor site for a 572-atom lattice with periodic boundary conditions and rms interatomic lattice coupling between the donor and lattice of 1/56 (black line), 1/28 (blue line), and 1/14 (dotted line). The $1/e$ decay in the probability scales approximately quadratically with coupling. The inset depicts the $t = 0$ boundary condition with the electron (darkened circle) localised on the dye (donor) molecule; (b) For comparison the back electron-transfer process is modelled assuming the electron is one lattice site removed (as shown in inset) from the dye and the dye-surface atom coupling is 1/3 the rms lattice coupling (very strong coupling to the dye). Once the wavefunction has localised in the solid-state there is little chance of back electron transfer from the band states.

than 3% (Spitler, 1987). The low quantum yield has generally been attributed to the inability of photogenerated majority carriers to escape the coulombic field of the parent cation (Onsager escape problem). However, there are numerous reasons and the other most probable explanation is poor surface quality. Defects and contaminants that act as trapping centres both decrease the coupling of the dye to the semiconductor band states and short-circuit the system. However, the SnS_2 forms very low defect surfaces that are atomically flat over large terraces. The high surface quality promotes intimate contact of dyes with the surface. This surface is the closest approximation to a homogeneous surface possible and forms an ideal test case for electron transfer involving weakly physisorbed molecules.

The excited-state lifetime of oxazine at this surface was found to be 40 ± 20 fs in contrast to nanosecond lifetimes observed in solution at an inert interface (Fig. 2.28). This significant decrease in lifetime was attributed to the new interfacial electron-transfer channel present at the SnS_2 surface. This assignment was confirmed by measuring the ground-state bleach, a direct observation of one of the main photo-products. This latter study determined the back-electron-transfer rates and that the short lifetime was not due to excited-state energy transfer or excitation of a charge-transfer band. The magnitude of the forward electron-transfer rate constant was outside the range of nuclear-mediated saddle point crossings; in other words, the dynamics are faster than either the solvent or intramolecular relaxation processes.

The exceptionally short lifetime prompted a re-examination of electron-transfer theory in the presence of an electronic continuum as the ‘bath’—in place of the conventional nuclear continuum. This analysis used the starting Hamiltonian, within the rotating wave approximation

$$\mathcal{H} = \sum_{j\alpha} |j\alpha\rangle E_{j\alpha} \langle j\alpha| + |k\beta\rangle E_{k\beta} \langle k\beta| + \sum_{j\alpha} |j\alpha\rangle V_{jk}^{a\beta} \langle k\beta| \quad (2.60)$$

where $E_{j\alpha}$ and $E_{k\beta}$ are the energies of the conduction-band states and dye state, respectively, and $V_{jk}^{a\beta}$ is the coupling between the discrete molecular state $k\beta$ and the conduction-band electronic states $j\alpha$.

The Liouville equation approach was employed to solve the corresponding density matrix, *i.e.*

$$\frac{d\rho'}{dt} = -i[\mathcal{H}, \rho'] = iL\rho' \quad (2.61)$$

where $L (= L_0 + L')$ is the Liouville operator corresponding to commutation of $\mathcal{H}$ with the operand and $L(\rho')$ is the complete molecular density matrix. Within this framework, it was shown analytically that the electron-transfer time is directly related to the electronic coupling, *i.e.*

$$k_{\text{ET}} = 4\pi\hbar V_o^2 \rho(E_j) \quad (2.62)$$

where V_o is the average electronic coupling between the molecular excited state basis and the band states. It was assumed that the band structure is isotropic and there is no significant $\mathbf{k}$ dependence within the relevant energy window. The term $\rho(E_j)$ is again an average density-of-states of the semiconductor within the energy range of the excited molecular levels. It should be noted that this reduces to a Fermi Golden Rule such that the effect of the semiconductor's density-of-states on the electron-transfer dynamics should be viewed as an effective coupling. Increasing or decreasing the

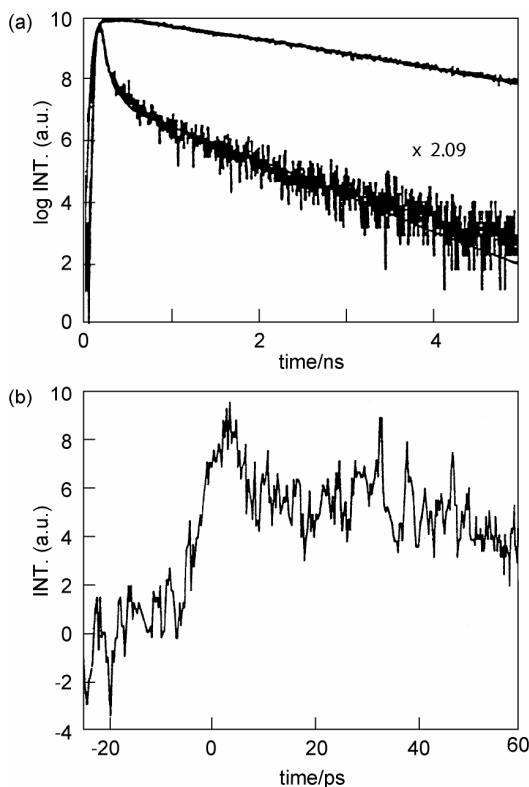


Figure 2.28 (a) Time-correlated single photon-counting studies of fluorescence from oxazine on a thin-film reference (upper curve) and on single crystals of SnS_2 (lower curve). Integration shows a fluorescence quenching ratio of nearly 10^5 in the presence of SnS_2 ; (b) femtosecond studies of the ground-state recovery of oxazine on SnS_2 using a pump-probe reflection geometry with sensitivity to changes in transmission of better than 10^{-6} . The ground-state recovery is position-sensitive and shows multi-exponential kinetics extending from 10 ps to several 100 ps arising from back electron transfer.

density-of-states (within the high density-of-states statistically averaged limit) only changes the electronic coupling per level and does not affect the dynamics. The terms $V_o^2 \rho(E_j)$ should be viewed as the effective electronic coupling between the dye and the semiconductor.

The most important point to note is that the electron-transfer process can be purely electronic. There are no nuclear motions required to sample the continuum states such that there is no fundamental limit (apart from defining the initial state) to the electron-transfer dynamics. This finding is in contrast to electron transfer to localised molecular states (Section 2.3.5). In this latter case, the solvent or intramolecular relaxation process dictates the rate of passage into the product channel.

The above analysis, showing that electron-transfer processes at dye-sensitised surfaces can involve purely electronic processes, helped rationalise the exceptionally fast electron-transfer time observed for oxazine at SnS_2 surfaces. Franck–Condon factors relating the nuclear wavefunction overlap to the transition probability between the reactant and product surfaces averages out of the problem. Basically, there are so many electronic levels involved that if one sums over all the open pathways the overlap integral goes to unity. There is always some electronic surface that is resonant with the vibronic/solvent coordinate of the excited dye. Within the classic Marcus description, the Franck–Condon modes of the intramolecular and intermolecular bath are thermally averaged and define the probability for the donor and acceptor electronic levels to achieve a resonance condition for electron exchange (point B in Fig. 2.24). This condition also defines the reaction saddle point, which is a narrow crossing point in the total nuclear configuration space for homogeneous (two-state) electron transfer. In contrast, for barrierless photoinduced electron transfer at dye-sensitised surfaces there is always an electronic state (acceptor) resonant with the dye excited electronic state for all nuclear displacements. Within the harmonic approximation employed in treatments of the bath coordinate, if there is no nuclear displacement required to stabilise the charge separation (the electronic continuum of the band serves this role), there is no reduction in the transition probability; the nuclear wavefunction overlap is unity. The point is illustrated schematically in Fig. 2.29.

The main conceptual advance made in the last few years is the acceptance that electron-transfer process at dye-sensitised systems under barrierless conditions can be purely electronic. A measurement of the nonradiative decay channel due to electron transfer under these conditions gives a direct determination of the electronic coupling. Subsequent to the initial work pointing this out, there have been a number of determinations of extremely fast electron-transfer times at dye-sensitised surfaces. For dye-derivatised TiO_2 electron-transfer times from 10 fs to 100 fs have been reported by a number of groups (Rehm *et al.*, 1996; Tachibana *et al.*, 1996; Hannappel *et al.*,

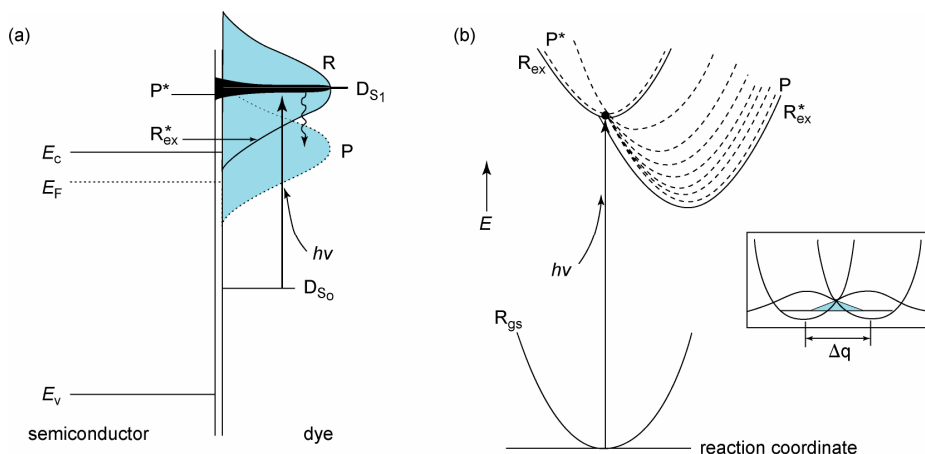


Figure 2.29 Electronic continuum energy diagram. (a) The photon absorption takes the system from the energetically unfavourable ground-state reactive surface (R_{gs}) of the dye to a barrierless excited-state reactive surface (R_{ex}); (b) the corresponding nuclear potential energy surface is shown. Each different electronic level within the conduction band mixes with the electronically excited state to create a reactive crossing. The reactant surface with the electron localised on the dye is shown as solid lines (only two given) and the product surfaces with the electron probability residing in the solid-state lattice depicted as dotted lines. The displacement between the reactant and product surfaces arises predominantly through intramolecular reorganisation of the dye and solvent modes with the change in charge density. The * denote surfaces that are energetically displaced from the most probable configurations for both product and reactant surfaces. The inset shows the nuclear overlap as a function of displacement (ΔQ) for harmonic oscillators. This overlap goes to unity if no displacement is required to stabilise the charge-separated state or there is a product surface intersecting all possible nuclear displacements along the reaction coordinate (as is the case with a wide acceptor bandwidth).

1997; Ghosh *et al.*, 1998; Martini *et al.*, 1998; Asbury *et al.*, 1999). This body of work establishes that electronic coupling between molecular states and bands of the solid-state can be appreciable—in the range of $100\text{--}1000\text{ cm}^{-1}$. This degree of electronic coupling would be considered adiabatic or strong coupling for electron-transfer processes to localised molecular states. This realisation is a very important advance. It takes us away from ideas based on the assumption of weak coupling to a new conceptual basis for fully exploiting interfacial charge-transfer. For example, the forward electron-transfer step can occur on exceptionally fast time scales—faster than nuclear relaxation processes. This means that non-thermal electron-transfer channels can be utilised to enhance the overall efficiency (by increasing the optical absorption bandwidth and generating hot electrons with sufficient energy to escape the coulombic barrier of the parent cation product state). Since the back electron-transfer process involves a molecular acceptor, nuclear relaxation is required to localise the

electron. This difference between the forward and back electron-transfer dynamics builds in a factor of 10^2 – 10^3 difference between the forward and back electron-transfer rates even under barrierless conditions for both processes. The magnitude of this difference is further enhanced by a nuclear activation barrier to the back electron-transfer step. This latter process occurs in the inverted Marcus regime. Relatively small barriers (≥ 0.1 eV) can increase the difference further by several orders of magnitude. Provided the excited dye level lies above the CBM and is in close proximity or direct contact with the surface, quantum yields of $> 99\%$ for photoanodic current are inherent to the transfer. The overall collection efficiency depends on other factors unrelated to the interfacial charge-transfer dynamics.

The following is a list of dynamical features salient to dye-sensitised surfaces:

1. The process involves majority-carrier injection. Thus it is very forgiving to defects and surface states. These are all filled, up to the Fermi level, and do not participate as traps.
2. The forward electron-transfer step can occur under exceptionally fast time scales—faster than nuclear relaxation. The fastest forward electron-transfer times will be realised with dyes that have excited-state surfaces above the CBM (barrierless conditions). For dyes in intimate contact (no intervening solvent or contaminant), the electron coupling can be in the 100 to 1000 cm^{-1} range (100 fs – 10 fs dynamics).
3. The excited state level should optimally lie more than the intramolecular reorganisation energy above the CBM ($\sim 0.3\text{ eV}$) to produce free carriers in the solid-state with sufficient excess kinetic energy to escape the coulombic barrier of the parent cation. This condition also ensures that all possible electronic states along the reaction coordinate are coupled to the conduction band. (Similar conditions hold for hole injection at *p*-type electrodes, where the ground state should lie $\sim 0.3\text{ eV}$ below the VBM.)
4. To be collected as photocurrent, the injected electron (majority-carrier) must escape the coulomb barrier imposed by the reaction field. This means that the injected carrier must spatially propagate outside the Onsager escape distance or dielectric screening length of the positively charged parent. Otherwise the carrier becomes effectively trapped in a fashion analogous to a carrier bound to a charge defect in semiconductors. The retarding field of the parent cation creates a significant barrier to charge separation local to the surface. Generally the system will undergo back electron transfer if the electron has insufficient kinetic energy to escape this field. This statement applies to a single photogenerated parent

cation. One has to consider the collective effect of the coulombic fields from each parent cation. Under normal illumination, many dye cation radical states are created. In order to avoid appreciable surface charging, the dye must be regenerated faster than the incident light flux generates parent cations. For example 10^{12} cm^{-2} dye cation radicals on III–V semiconductor would produce a 1 eV field opposing current collection—an order of magnitude increase in the coulombic barrier over a single-particle description.

5. The back-electron-transfer step is identical to the band-to-molecular state charge-transfer process involving minority-carrier injection (Section 2.3.5). This step is sensitive to defects that would act as donors with smaller activation barriers than a single regeneration step involving band-to-molecular acceptor transitions. Optimally the surface should have low defect densities and the cation level should lie as high above the valence band as possible (electrochemical determinations of the redox potential of the cation radical are needed).

Overall the forward electron-transfer step must be much faster than all other photophysical decay mechanisms of the dye's excited state. The forward electron-transfer time should be $>10^2$ faster than the back-electron-transfer dynamics. The regeneration of the dye must be faster than both back electron transfer and the rate of photoinduced surface charging. The mechanism of regeneration and ensuing dynamics determines the required conditions for the back-electron-transfer rates.

2.5 Conversion of solar energy

The conversion of solar energy into electrical energy and the formation of a storable fuel such as hydrogen by using semiconductor liquid junctions were initiated in the 1970s. Hundred of papers have been published and the results have been summarised in various articles (Gerischer, 1979; Nozik, 1979; Wrighton, 1979; Tributsch, 1982, 1986; Parkinson, 1983; Rajeshwar, 1983; Hodes, 1985; Memming, 1988, 1990; Lewis, 1990, 1995; Koval and Howard, 1992; Nozik and Bard and Fox, 1995 and Memming, 1996).

2.5.1 Electrochemical photovoltaic cells

In principle, electrochemical photovoltaic cells (also known as regenerative solar cells) can be constructed very simply. They consist of a semiconductor electrode, an electrolyte containing a redox system and a counter electrode, as illustrated in the lower part of Fig. 2.30. The energy scheme for a cell with an *n*-type semiconductor and a redox system with a standard potential close to the valence band is shown in the upper part of Fig. 2.30. On illumination of such a cell, holes are created and transferred to the reduced species of the redox couple. The electrons reach the ohmic contact on the backside of the semiconductor, traverse the external circuit, do useful work, and reach the counter electrode, at which they reduce the oxidised component

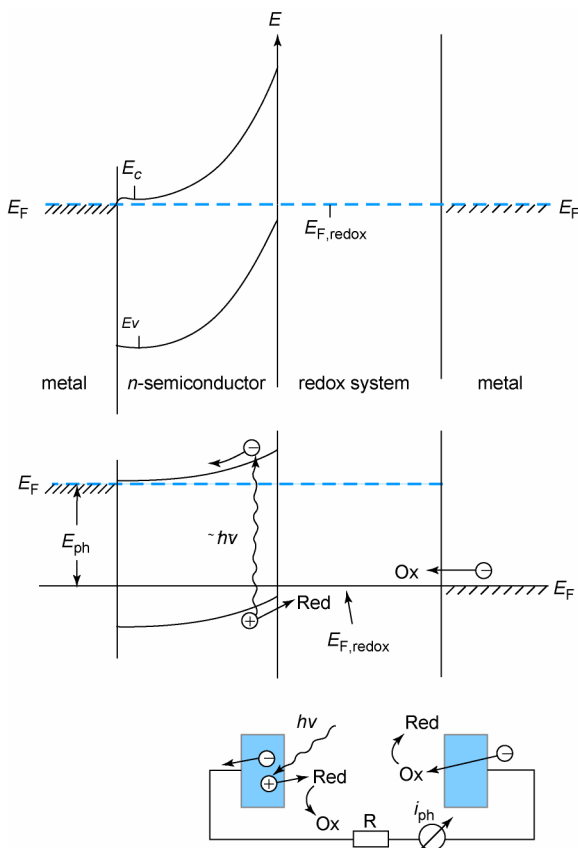


Figure 2.30 Energy-level scheme and cell half-cell reactions for a semiconductor | redox system | metal electrochemical photovoltaic cell.

of the redox couple. Since no net consumption of the material in the electrolyte occurs, this cell works under regenerative conditions. The current–potential behaviour of a semiconductor–liquid junction has already been derived in Section 2.3 resulting in eqs. 2.57 and 2.58. The same type of equation can be used for a complete cell provided that the exchange current at the counter electrode is sufficiently large. We have then

$$i = -i_o \left[\exp \left(-\frac{q(U - U^\circ)}{\beta kT} \right) - 1 \right] + i_{ph} \quad (2.63)$$

where β is the ideality factor. Instead of the overvoltage η , U is used here for the cell voltage V as measured between the back contact of the semiconductor and the counter electrode. Equation 2.63 is also valid for pure solid-state devices such as semiconductor–metal contacts (Schottky junctions) and p – n junctions. The physics of the individual contacts is contained in i_o . The latter two systems differ insofar as the forward current in the first is carried by majority carriers (majority-carrier device) whereas the second is a minority-carrier device. A photoelectrochemical cell can be of either type. If majority carriers control the forward current then the kinetics of electron transfer determine i_o , which is given by eq. 2.43. In the case of a minority-carrier device, i_o is given by eq. 2.49. Most systems studied so far are majority-carrier devices because minority-carrier injection into a semiconductor electrode can only be achieved if the standard redox potential is very close to the valence band of an n -electrode, as *e.g.* in the case of the $\text{Cu}^{1+}/\text{Cu}^{2+}$ -couple at n -GaAs (Reineke and Memming, 1992). Concerning the ideality factor β in eq. 2.63, it should be unity for a majority-carrier device. This condition has been reasonably well fulfilled when using aprotic solvents (see Fig. 2.20). In principle, a photoelectrochemical cell can also be made by using a p -type electrode and a redox system where the standard potential is close to the conduction band. Unfortunately, not many p -type materials are available and there is only one report on cells containing p -InP (Heller *et al.*, 1981).

Besides the photocurrent, the photovoltage of a photovoltaic cell is of importance. It is obtained for $i = 0$, *i.e.*, $U = U_{ph}$. We have then

$$U_{ph} = -\frac{\beta kT}{q} \ln \left(\frac{i_{ph}}{i_o} + 1 \right) \quad (2.64)$$

The maximum conversion efficiency η_{mp} of a photovoltaic cell is defined as

$$\eta_{mp} = P_{mp} / P_o \quad (2.65)$$

in which P_o is the power of incident sunlight and P_{mp} is the maximum output power,

given by

$$P_{\text{mp}} = i_{\text{mp}} V_{\text{mp}} \quad (2.66)$$

The quality of a photovoltaic cell is characterised by the so-called fill factor, defined as

$$\eta_{\text{fill}} = \frac{i_{\text{mp}} V_{\text{mp}}}{i_{\text{ph}}^{\text{sc}} V_{\text{ph}}^{\text{oc}}} \quad (2.67)$$

where $i_{\text{ph}}^{\text{sc}}$ and $V_{\text{ph}}^{\text{oc}}$ are the short-circuit current and open-circuit voltage, respectively. In many cases, instead of a complete i - V curve, the photocurrent i_{ph} is plotted versus the photovoltage V_{ph} as a power plot. The latter is obtained by connecting the semiconductor and the counter electrode through a load resistance (as in the lower part of Fig. 2.30) that is varied from infinity to zero.

It is the aim of the research in this area to produce cells with large photocurrents and high photovoltages in order to achieve a high conversion efficiency. According to eq. 2.53 a sufficiently large i_{ph} is obtained if the penetration depth ($1/\alpha$) of light is small, so that most of the incident light is absorbed within the space-charge region ($1/\alpha \leq w_{\text{scl}}$) or at least within the diffusion length of the minority carriers ($1/\alpha \leq L_p$). On the other hand, the photovoltage depends not only on i_{ph} but also on i_o (eq. 2.64). In order to maximise V_{ph} , i_o must be minimised. In the case of a minority-carrier device, i_o is entirely determined by properties of the semiconductor (eq. 2.49). Within limits it may be possible to reduce the donor density to an appropriate value. As already discussed, most systems are majority-carrier devices and i_o is then determined by the transfer kinetics (eq. 2.43). As discussed in Section 2.3.2, the corresponding rate constant is extremely large in several cases, so that thermionic emission controls the current, as in Schottky junctions (Fig. 2.20). Those systems should be avoided. Reasonable photovoltages of about 0.8 V can be expected with $i_{\text{ph}} = 30 \text{ mA cm}^{-2}$ and $i_o \approx 10^{-14} \text{ A cm}^{-2}$ (eq. 2.30). The latter can be achieved with $k_{\text{c}}^- = 10^{-18} \text{ cm}^4 \text{ s}^{-1}$, assuming $\phi_{\text{sc}}^0 = 0.7 \text{ V}$ (eq. 2.38). To obtain a high conversion efficiency it is also important to have a high fill factor (eq. 2.67). This condition implies rather ‘rectangular’ current–voltage curves. This can only be achieved with systems where the log i - V curves show a slope close to 60 mV per decade. Although H_2O would be the simplest solvent, the latter condition seems to be difficult to fulfil in aqueous media. In addition, anodic decomposition is a severe problem in aqueous solutions.

During the last two decades, many regenerative cells have been investigated and energy conversion efficiencies of up to 16% have been reported. Memming (1990, 2000) gives overviews. Table 9.1 at the end of Chapter 9 gives performance parameters for regenerative cells containing different types of semiconductors.

2.5.2 Photoelectrolysis of water

The efficient photoelectrolysis of water into hydrogen and oxygen using sunlight has been an objective of many researchers since the early 1970s. The photoelectrolysis of H_2O can be performed in cells that are similar to the regenerative cells described in Section 2.4.1. Figure 2.31 illustrates the energy scheme of the corresponding system (n -type semiconductor| H_2O |counter electrode). The two electrodes, semiconductor and counter electrode, are short-circuited. In the case of an n -type electrode, the holes created by light excitation must react with H_2O resulting in O_2 formation whereas at the counter electrode H_2 is produced. The electrolyte can be described by two redox potentials, $U^\circ(\text{H}_2\text{O}/\text{H}_2)$ and $U^\circ(\text{H}_2\text{O}/\text{O}_2)$, which differ by 1.23 eV. At equilibrium (left-hand side of Fig. 2.32), the electrochemical potential (or Fermi level) is constant in the whole system and occurs somewhere between the two standard energies $U^\circ(\text{H}_2\text{O}/\text{H}_2)$ and $U^\circ(\text{H}_2\text{O}/\text{O}_2)$. Its position depends on the relative concentrations of H_2 and O_2 . The two reactions, O_2 formation at the n -type semiconductor and H_2 formation at the counter electrode, can obviously only occur if the bandgap of the semiconductor is >1.23 eV, and the conduction band edge is negative of $U^\circ(\text{H}_2\text{O}/\text{H}_2)$ while the valence band edge is positive of $U^\circ(\text{H}_2\text{O}/\text{O}_2)$. At equilibrium, the Fermi level within the metal is below $U^\circ(\text{H}_2\text{O}/\text{H}_2)$ so that H_2O cannot be reduced in the dark. Since the metal electrode is short-circuited with the semiconductor, the majority quasi-Fermi level remains constant in both electrodes during illumination. The energy bands are flattened on light excitation until the Fermi level in the metal is moved above $U^\circ(\text{H}_2\text{O}/\text{H}_2)$ so that electron transfer to H_2O becomes possible.

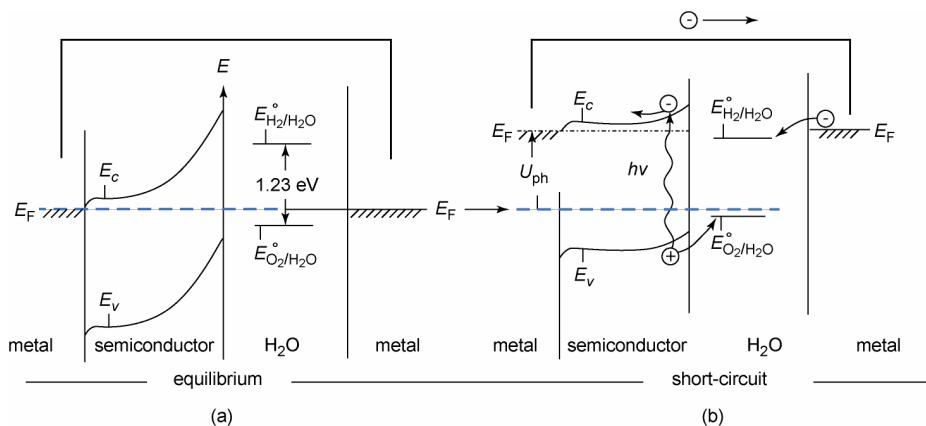


Figure 2.31 Energy level scheme for a photoelectrolysis cell (a) at equilibrium; (b) under illumination.

According to this cell design, only semiconductor electrodes that are initially stable can be used. It is quite easy to produce H_2 ; however, many low-gap n -type materials are not applicable because anodic decomposition occurs instead of O_2 formation. There are several oxide semiconductors that show sufficient stability (Fujishima and Honda, 1972). However, few meet the energetic requirements and these few have relative large bandgaps, *e.g.*, $SrTiO_3$ ($E_g = 3.3$ eV). The efficiency of H_2O cleavage is then very low since only UV light can be absorbed (Mavroides *et al.*, 1976). The only low-gap n -type semiconductor at which O_2 formation was found is RuS_2 ($E_g = 1.3$ eV). This is a d -band transition metal chalcogenide with which only rather slow decomposition kinetics were observed. Unfortunately, this material did not fulfil the energetics prerequisites as a large downward shift (1.8 eV) of the energy bands was found on illumination (Kühne and Tributsch, 1986), as also observed for WSe_2 (Fig. 2.15). The final position of the conduction band was far below $U^\circ(H_2O/H_2)$ so that H_2 formation was only possible by applying an external voltage (Tributsch, 1985). The stability against corrosion was ascribed to the formation of a few monolayers of RuO_2 (Jaegermann and Tributsch, 1988). Since RuO_2 is a metallic conductor, a Schottky junction was probably formed (Memming, 1990).

A variety of other systems have been suggested and some were also tested such as cells containing an n -semiconductor anode and a p -type cathode, photoelectrolysis cells integrated with photovoltaic configurations, and tandem and cascade type of cells (Nozik and Memming, 1996).

2.5.3 Conversion efficiencies

In Section 2.4.1, we saw how the photovoltage of a photoelectrochemical cell can be maximised. There is, however, a thermodynamic limit, often called the detailed balance limit, on the photovoltage and consequently of the conversion efficiency. Corresponding theories have been published (Ross and Hsiao, 1977; Ross and Collins, 1980; Bolton *et al.*, 1980). These theories are applicable for photovoltaic cells as well as for photoelectrolysis cells, and yield a lower limit of a recombination rate which cannot be surpassed. The basic concept of the theory is as follows. At equilibrium in the dark, the recombination flux $j_{r, \text{dark}}$ of radiative transitions across any plane in an ideal cell is equal to the photon flux j_{bb} emitted by unit surface area of a blackbody, *i.e.*

$$j_{r, \text{dark}} = j_{bb} = \int (2\pi c n_r^2 / \lambda^4) \left[\exp\left(\frac{hc}{\lambda kT}\right) - 1 \right]^{-1} \sigma(\lambda) d\lambda \quad (2.68)$$

where c is the velocity of light, λ the wavelength, n_r the refractive index of the black body and $\sigma(\lambda)$ the (dimensionless) absorption probability: $\sigma(\lambda) = 1$ for $\lambda \leq \lambda_g$; $\sigma(\lambda) = 0$ for $\lambda > \lambda_g$. Assuming that the radiative recombination flux j_r in the light is proportional to $(np - n_i^2)$ in the illuminated (non-equilibrium) cell, this flux is given by

$$j_r = j_{bb} \exp\left(\frac{\tilde{\mu}}{kT}\right) \quad (2.69)$$

where $\tilde{\mu}$ is the difference between the quasi-Fermi levels of electrons and holes. Equation 2.69 is always valid for thermalised hole–electron populations because it can be derived from the first and second laws of thermodynamics (Ross, 1966, 1967; Bolton *et al.*, 1980). The excitation rate of the illuminated absorber (semiconductor) is given by

$$j_e = \int j_\lambda^0 \sigma(\lambda) d\lambda \quad (2.70)$$

where j_λ^0 is the incident spectral photon flux. The maximum difference of the two quasi-Fermi levels, $\tilde{\mu}_{\max}$, is obtained when $j_e = j_r$. Then with eq. 2.69 we have

$$\tilde{\mu}_{\max} = kT \ln\left(\frac{j_e}{j_{bb}}\right) \quad (2.71)$$

This difference of quasi-Fermi levels corresponds to the maximum photovoltage that can be obtained with a solar cell with a thermalised excited-state population. Evaluating eq. 2.71 shows that the maximum photovoltage is always considerably smaller than the bandgap. For example, for GaAs ($E_g = 1.4$ eV), $\tilde{\mu}_{\max} = 0.9$ eV. Combining an n -GaAs electrode with a redox couple where the standard potential is close to the valence band (Fig. 2.30), a band bending of about 0.5 eV remains under illumination.

More important, however, is the output power of a solar cell. As illustrated in Fig. 2.32, the photovoltage is somewhat lower under maximum-power conditions, and instead of $\tilde{\mu}_{\max}$ we then have $\tilde{\mu}_{\text{mp}}$. According to Ross and Hsiao (1977), one obtains for the maximum power

$$P \approx j_e \left(1 - \frac{kT}{\tilde{\mu}_{\max}}\right) \tilde{\mu}_{\text{mp}} \quad (2.72)$$

with

$$\tilde{\mu}_{\text{mp}} \approx \tilde{\mu}_{\max} - kT \ln\left(\frac{\tilde{\mu}_{\max}}{kT}\right) \quad (2.73)$$

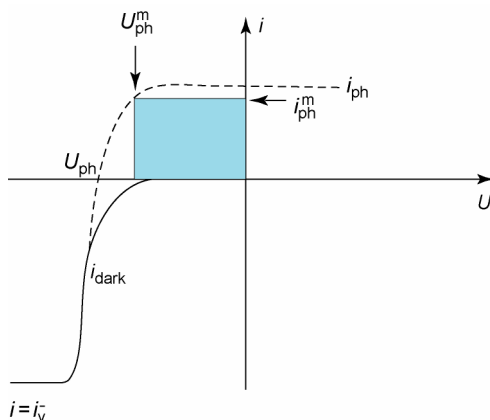


Figure 2.32 Current–potential curve in the dark and under illumination for an electrochemical photovoltaic cell.

Assuming that all minority carriers created by light excitation are transferred across the interface (quantum efficiency of unity), then $i_{ph} = qj_e$ is the photocurrent density of the cell. Using eqs. 2.70–2.73, the maximum power expected for a photovoltaic cell can be calculated for semiconductors of different bandgaps. As shown by the dashed curve in Fig. 2.33, the highest efficiency is 28% at $E_g = 1.2$ eV.

The theory of Ross *et al.*, derived for radiative transitions can be extended to radiationless recombinations. It is assumed here that at equilibrium electron–hole pairs are also created by electron–phonon interaction. The same type of interaction is considered for the recombination process. On the basis that its rate increases exponentially with difference of the quasi-Fermi levels—an assumption which does not follow from the first principles in thermodynamics—the recombination current i_r is given by Ross and Collins (1980) as

$$i_r = \gamma q j_{bb} \exp\left(\frac{\tilde{\mu}}{kT}\right) \quad (2.74)$$

where γ is the ratio of radiationless to radiative transitions (*cf.* eq. 2.69). Thus radiationless recombination can substantially reduce photovoltage and efficiency.

If energy is to be stored in a chemical fuel, for instance by producing H_2 via the photoelectrolysis of H_2O , further energy losses due to overpotentials have to be encountered. The two overpotentials, η_{ox} and η_{red} , are defined as the difference between the quasi-Fermi level and the corresponding redox potential. Using eq. 2.72, the conversion efficiency for the production of a chemical fuel is then given as

$$\eta_{\text{conv}} = \frac{P_{\text{stor}}}{P_0} = \frac{j_{\text{ph}}}{P_0} \left(1 - \frac{kT}{\tilde{\mu}_{\text{max}}} \right) \tilde{\mu}_{\text{stor}} \quad (2.75)$$

where $\tilde{\mu}_{\text{stor}}$ is the storable energy. Here it is assumed that

$$\tilde{\mu}_{\text{mp}} \geq \tilde{\mu}_{\text{stor}} + q\eta_{\text{ox}} + q\eta_{\text{red}} \quad (2.76)$$

On the other hand, $P_{\text{stor}} = 0$ for

$$\tilde{\mu}_{\text{stor}} + q\eta_{\text{ox}} + q\eta_{\text{red}} > \tilde{\mu}_{\text{max}} \quad (2.77)$$

In the small range between $\tilde{\mu}_{\text{mp}}$ and $\tilde{\mu}_{\text{max}}$, we have (Memming, 1990)

$$P_{\text{stor}} = j_{\text{ph}} \left[1 - \exp \left(\frac{\tilde{\mu}_{\text{stor}} + q\eta_{\text{ox}} + q\eta_{\text{red}} - \tilde{\mu}_{\text{max}}}{kT} \right) \right] \tilde{\mu}_{\text{stor}} \quad (2.78)$$

This equation is obtained by using eqs. 22 and 23 from Bolton *et al.* (1980). In the range where eq. 2.78 is valid, the quasi-Fermi level difference $\tilde{\mu}$ should be as small as possible in order to avoid recombination losses, *i.e.*, $\tilde{\mu} = \tilde{\mu}_{\text{stor}} + q\eta_{\text{ox}} + q\eta_{\text{red}}$. Figure 2.33 gives corresponding values for the photoelectrolysis of water ($\tilde{\mu}_{\text{stor}} = 1.23$ eV) as a function of the semiconductor bandgap for different overvoltages. The curves in Fig. 2.33a were calculated for a cell consisting of a semiconductor and metal counter electrode, both being short-circuited. The data in Fig. 2.33b are for a system in which H_2O is cleaved by reduction at a *p*-electrode and by oxidation at an *n*-electrode in a two-photon process. In both cases, the efficiency decreases with increasing overpotential. Theoretically, the efficiency can be increased up to 67% in multiphoton devices (Bolton *et al.*, 1985). Ross and Nozik (1982) reported the same theoretical limit for a perfect hot-carrier photon converter.

2.5.4 Competition between redox reactions and anodic decomposition

The lack of photostability of *n*-type semiconductor electrodes is a severe problem when using aqueous solutions. Holes excited by light excitation and then driven toward the surface can be either used for the decomposition or are transferred to a redox system. In the case of large band-gap oxides, the stability is thermodynamically controlled; *i.e.* the anodic decomposition occurs only at potentials that are considerably more positive than typical redox reactions. In all other cases, the competition between these two processes is kinetically controlled (Memming, 1990, 1994). In several cases, a decrease of the stability of *n*-type semiconductors with increasing

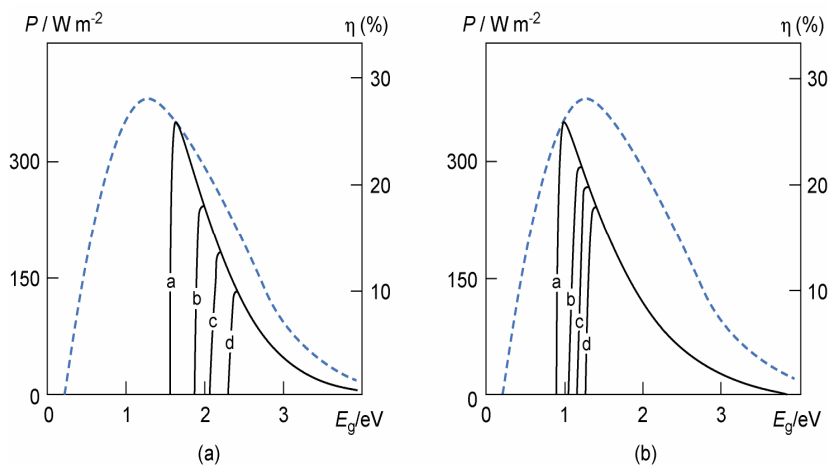


Figure 2.33 Theoretical conversion efficiencies for photoelectrochemical H_2O cleavage; (a) n -type electrode combined with a metal counter electrode; (b) n -type electrode short-circuited with a p -type electrode of equal bandgap. Calculated for different overvoltages of (a) 0.0 V; (b) 0.3 V; (c) 0.5 V; (d) 0.7 V. Source: Memming (1990).

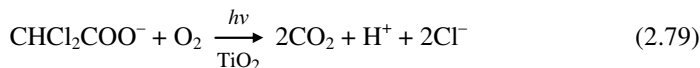
light intensity was observed (Frese *et al.*, 1980; Overmeire *et al.*, 1980; Gomes *et al.*, 1981). Rather complex kinetic models, which will not be discussed here, were developed to explain this effect (Cardon *et al.*, 1980; Gerischer and Lübke, 1983; Memming, 1994). Since the kinetics may also be controlled by the surface chemistry and surface structure, it is very difficult to predict whether corrosion or a redox process will dominate under given circumstances. Further quantitative studies should not be restricted to the corrosion of n -electrodes. Additional investigations with the corresponding p -electrodes can give more insight into these reactions because corrosion and oxidation of a redox system are then majority-carrier processes. Reactions at p - and n -electrodes can then easily be compared by applying the quasi-Fermi level concept.

The transition metal chalcogenides such as n -WSe₂ are a particular class of electrode materials, and their photoelectrochemical behaviour is of interest from the fundamental point of view. If the basal planar surfaces (perpendicular to the c -axis) with a low density of steps are contacting the electrolyte, these layered materials are relatively stable. Since the corrosion rate is very small, the anodic photocurrent occurs at a high overvoltage with respect to the flatband potential in the dark. As discussed in Section 2.3.1 (Fig. 2.15), the flatband potential U_{fb} is shifted on illumination because holes accumulate at the surface. On addition of a redox couple such as $[\text{Fe}(\text{phen})_3]^{2+/3+}$

U_{fb} and the energy bands at the surface remained unchanged. The photocurrent that now develops near $U_{fb}(\text{dark})$ (Fig. 2.15) is entirely due to the oxidation of $[\text{Fe}(\text{phen})_3]^{2+}$ and the electrode remains completely stable (Sinn *et al.*, 1990).

2.6 Photocatalysis

In Section 2.4, we described systems in which solar energy is used for producing electric energy or a storable fuel. For instance, solar energy is used in a photoelectrolysis cell for producing H_2 as a storable fuel. Both processes lead to an increase of free energy, *i.e.* $\Delta G > 0$ (uphill reaction). On the other hand, a photocatalytic reaction is a downhill reaction $\Delta G < 0$ where light excitation is used only to speed up a reaction. Examples are the mineralisation or the detoxification of organic waste, as discussed by Serpone and Emeline in Chapter 5. A typical model substance is dichloroacetate, and Bahnemann *et al.* (1991) give its oxidation as



The oxidation of acetate by O_2 is a downhill reaction, which is catalysed by TiO_2 in the presence of light absorbed by the semiconductor. Corresponding reactions are performed with stable oxides, primarily with TiO_2 particles. The basic processes are illustrated in Fig. 2.34 for dispersed small semiconductor particles as typically used in this application. The holes produced by light excitation are used for the oxidation of the acetate, whereas electrons are transferred to O_2 .

In contrast to semiconductor electrodes, the particles cannot be polarised: in the terminology of electrodes, all reactions occur at open-circuit conditions. Accordingly, two reactions—reduction of an electron acceptor and oxidation of a pollutant molecule—always occur simultaneously. The slowest process determines the overall reaction rate. Since undoped TiO_2 particles of a size smaller than $1\ \mu\text{m}$ are usually used, their thickness is smaller than the theoretical thickness of the space-charge layer; *i.e.* there is no electric field within the particle for separating electron–hole pairs. Accordingly, the quantum efficiency of the reaction depends only on the transfer rates at the interface, the recombination rates and the transit time τ , the latter being given by Grätzel and Frank (1982)

$$\tau = R^2 / \pi^2 D \quad (2.80)$$

where R is the particle radius and D the carrier diffusion coefficient. Taking typical values of $D \approx 0.1\ \text{cm}^2\ \text{s}^{-1}$ and $R \approx 0.5\ \mu\text{m}$, the average transit time τ is $\sim 1\ \text{ns}$.

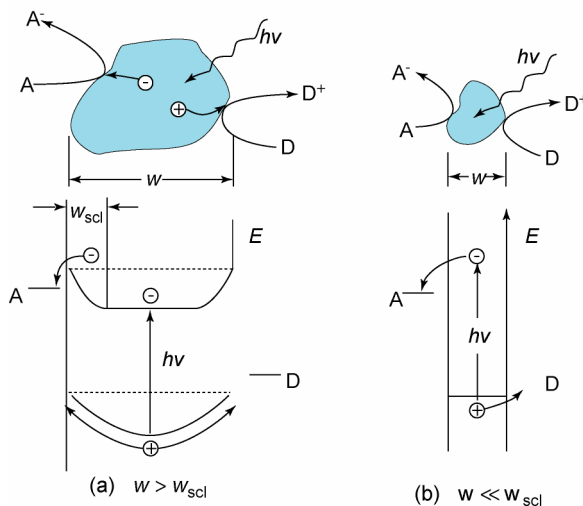


Figure 2.34 Electron and hole transfer between (a) large or (b) small semiconductor particles and electron acceptor A and donor D.

The photodegradation of many organic compounds has been studied (Ollis, 1985; Heller, 1995; Hoffman *et al.*, 1995). The reaction mechanism has been studied only in few cases. It has been a controversial question, as discussed in Chapter 5, whether the first step in the oxidation of the organic compound is due to direct hole transfer or whether an OH radical is first formed which then oxidises the organic molecule. In this context, investigations by laser flash experiments performed with TiO_2 colloids are of special interest. Transient absorption spectra have been obtained which were related to trapped holes and electrons with absorption maxima around 430 and 620 nm, respectively (Bahnmann *et al.*, 1984). Later investigations have shown that the trapping, especially of the electrons, occurs within few picoseconds after the flash (Rothenberger *et al.*, 1985; Serpone *et al.*, 1995). In the presence of O_2 , the lifetime of the trapped electrons decreased; *i.e.* O_2 is reduced by these trapped electrons. The situation is completely different for the oxidation process. Here the absorption of trapped holes is strongly reduced but their lifetime (*ca.* 40 μs) remained unchanged on addition of a hole scavenger such as dichloroacetate. Accordingly, dichloroacetate is not oxidised by trapped holes. Since fewer holes are obviously trapped, the oxidation must occur via free holes (Bahnmann *et al.*, 1997). This must be a very fast process so that only adsorbed molecules can be oxidised.

Whether the anodic or the cathodic reaction is rate-limiting has not yet been determined. Recently, it has been shown that the role of oxygen is actually twofold;

first O_2 is an electron acceptor; second, O_2 is required in the oxidation process itself. This has been illustrated for reactions of aliphatic compounds at TiO_2 particles (Hoffmann *et al.*, 1995). Serpone and Emeline give further details in Chapter 5.

2.7 Summary

This chapter is intended to serve as a basis for understanding the reviews given throughout this volume. It has provided an overview of essentially all the fundamental processes governing the conversion of solar energy into other forms of energy based on exploiting semiconductor photochemistry.

Section 2.2 has given an up-to-date account of the operating photophysical processes. In this regard, it is really only in the last five years that it has been possible completely to characterise the different relaxation pathways of photoexcited charge carriers with sufficient time resolution to enable a rigorous connection of the relaxation dynamics to energy conversion efficiency. In order to maximise the stored energy, all heat-producing channels should be minimised to avoid entropic losses to the energy-conversion processes. Under depletion conditions typical of bulk semiconductor–liquid junctions, the dominant thermalisation process is electron–phonon scattering. This process can be controlled to a certain degree by using quantum confinement and attention to surface-defect densities to reduce the density of electronic states. The analogous process of solvent relaxation that is responsible for promoting the charge-transfer process (semiconductor donor/molecular acceptor processes) has been found to occur on very similar time scales to electron–phonon scattering. In fact, for small-molecule, polar liquids such as water and acetonitrile, the solvent relaxation mediated through inertial motions can be an order of magnitude faster than electron–phonon thermalisation processes in the solid state. However, the most important recent advance in our understanding of the operating dynamics is that the electronic coupling between molecular acceptors/donors and the bands of the solid state can occur within the adiabatic coupling limit. With our new understanding of the solvent response and effect of the solid-state electronic continuum on the reaction coordinate, it is apparent that the dynamics of interfacial charge transfer can be competitive with even the fastest solid-state relaxation processes. This new level of understanding will hopefully lead to new strategies for optimising energy conversion.

These microscopic details have to be viewed in the context of the entire electrochemical system, as outlined in Section 2.3. The energetics of the interface in relation to electrochemical measurements and solid-state conventions have been given. The energetics provide a guideline for determining the maximum energy

conversion and the driving force for the energy transduction process, however, defined. This information, in combination with the concept of quasi-Fermi levels to include the effect of light absorption on the carrier distributions, can be connected to the steady-state photocurrent and photovoltages. Ultimately, it is the current flux across the interface that is responsible for energy transduction to either work or stored (electrical or chemical) energy, as described in Sections 2.4 and 2.5. To understand the overall energy conversion, one has to keep in mind the microscopic dynamics discussed in Section 2.2 and the joint density of (donor/acceptor) states that enable charge redistribution, as discussed in Section 2.3 within the context of electrochemical observables. This latter distribution of states has been treated using Fermi statistics for the solid state and assuming linear response for the solvent coordinate with respect to the reorganisation energy and associated nuclear activation barrier for a given redox potential. Continuum theories provide useful estimates of the reorganisation energies for this purpose but were not discussed at any depth. There have been significant strides in attaining more accurate microscopic descriptions (*e.g.* Calhoun and Voth, 1998) that will undoubtedly provide more rigorous guidelines in future.

The one aspect of the problem that has not been covered in detail is the structural nature of the interface. Chemically controlling the interface through quantum confinement effects and specifically designing the interface to differentially stabilise the charge-transfer process along a desired pathway is clearly the way of the future. It is hoped that the background provided here will help collate the diverse phenomena to be discussed in the other chapters and provide the basic principles for attaining such molecular-level control for fully optimising solar energy conversion strategies.

Editorial note

The authors submitted the final version of this manuscript in 2001. Owing to subsequent delays in the preparation of this book series, most of the references in this chapter date from this time. This chapter provides the fundamental photophysics and photoelectrochemical basics that are still relevant. Updated references, where needed, have been provided by the editors.

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CHAPTER 3

FUNDAMENTALS AND APPLICATIONS OF QUANTUM-CONFINED STRUCTURES

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Atoms on a small scale behave like nothing on a large scale, for they satisfy the laws of quantum mechanics. So, as we go down and fiddle around with the atoms down there, we are working with different laws, and we can expect to do different things. We can use some system involving the quantized energy levels.

Richard P. Feynman, December 1959.

3.1 Introduction

In this chapter, we consider solar power either in the form of electricity produced by photovoltaic cells or in the form of stored chemical potential in liquid or gaseous fuels. For the latter, examples are hydrogen, alcohol, or hydrocarbons produced using solar photons to split water into its elements or to drive the reaction of carbon dioxide and water to yield reduced carbon compounds and oxygen (*i.e.* artificial photosynthesis). The cost of solar power is determined by the conversion efficiency (η) of the solar converter and its total capital cost per unit area. The ratio of the capital cost per unit area ($\$/\text{m}^2$) to the peak power (W_p) produced per unit area yields the generated solar power cost in units of $\$/\text{peak watt}$ ($\$/W_p$), where W_p is the peak solar power density (watts/unit area) delivered by the device at the surface of the Earth at high noon with no clouds ($W_p = \eta \times 1000 \text{ W/m}^2$). To convert $\$/W_p$ to $\$/\text{kWh}$ an approximate conversion is simply to multiply $\$/W_p$ by a factor F that ranges from 0.03 (www.solarbuzz.com) to 0.05 (Surek, 2005) and takes into account the total insolation per year at a given site on Earth (*i.e.* integrated irradiance over the diurnal cycles and historical cloud cover), interest rates, the system lifetime, depreciation, operating costs, and maintenance; here we use an average value of $F = 0.04 \text{ kWh}/W_p$.

To achieve massive utilisation of solar power on the terawatt (TW) scale (the total energy consumed globally in 2006 was about 13 TW-yr), it is necessary to develop solar conversion systems that are cost-competitive not only with the present cost of electricity derived from coal and nuclear energy, but also with liquid and gaseous fuels derived from fossil sources. In 2007, electricity cost around 0.07–0.10 \$/kWh and the average cost of gaseous and liquid fuel produced from natural gas and petroleum is between 7–14 \$/MMBtu (0.02–0.04 \$/kWh) (see www.eia.doe.gov). The present cost of photovoltaic systems ($\sim$ \$5.00 for the PV module plus $\sim$ \$3.00 for the balance-of-systems cost) is $\sim$ 7–9 $\$/W_p$, which is equivalent to about $\$8/W_p \times 0.04 \text{ kWh}/W_p = 0.32 \text{ $/kWh}$. Thus, to achieve a solar power cost competitive with fossil-derived liquid and gaseous fuels, as well as fossil or nuclear electricity, the cost needs to be in the range of 0.02–0.04 \$/kWh or $\sim 0.03/F \sim \$0.75/W_p$ for the system (and $\sim \$0.40/W_p$ for the module); for PV this represents greater than a tenfold decrease in cost from present-day (2007) systems. To meet this goal, the conversion system has to have both high efficiency and low cost/unit area. Thus, for example, if the total system areal cost can be reduced to $\$150/\text{m}^2$ from the present cost of $\sim \$800/\text{m}^2$, then the module conversion efficiency needs to be 37.5%. Since the module efficiency is about 75% of the individual cell efficiency, the cell efficiency needs to be about 50% for an areal cost of $\$150/\text{m}^2$.

As is well known, the maximum thermodynamic efficiency or so-called ‘detailed balance limit’ for the conversion of unconcentrated solar energy into electrical free energy in a single-threshold absorber was calculated by Shockley and Queisser (1961) to be about 31%; this analysis is also valid for the conversion of unconcentrated solar energy to chemical free energy (Ross, 1966 and 1967). This calculation was based on several constraints: (1) the only loss of photogenerated electrons and positive holes (charge carriers) is through radiative recombination (this is termed the radiative limit); (2) detailed balance is assumed; (3) a maximum yield of one electron–hole pair per absorbed photon is produced; and (4) thermal equilibrium is attained between electrons and phonons. The 31% maximum efficiency value is attainable in semiconductors with bandgaps ranging from about 1.2 eV to 1.4 eV. However, the solar spectrum contains photons with energies ranging from about 0.5 eV to 3.5 eV. Photons with energies below the semiconductor bandgap are not absorbed, while those with energies above the bandgap create electrons and holes with a total excess kinetic energy equal to the difference between the photon energy and the bandgap. This excess kinetic energy creates an effective temperature for a Boltzmann ensemble of the photogenerated carriers that can be much higher than the lattice temperature after the electrons and holes have equilibrated (thermalised) among themselves. Such carriers are termed ‘hot electrons and hot holes’, and the initial carrier temperature on

photon absorption can be as high as 3000 K with the lattice temperature at 300 K. In bulk semiconductors, the division of this kinetic energy between electrons and holes is determined by their effective masses, with the carrier having the lower effective mass receiving more of the excess energy (Nozik, 2001b). Thus

$$\Delta E_e = (h\nu - E_g) \left[1 + m_e^* / m_h^* \right]^{-1} \quad (3.1)$$

$$\Delta E_h = (h\nu - E_g) - \Delta E_e \quad (3.2)$$

where ΔE_e is the energy difference between the conduction band and the initial energy of the photogenerated electron, and ΔE_h is the energy difference between the valence band and the photogenerated hole (see Fig. 3.1).

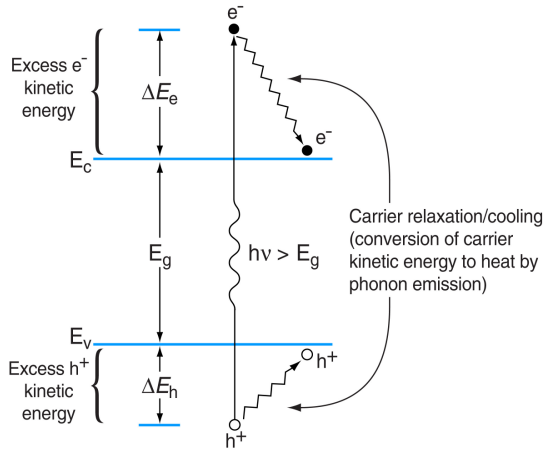


Figure 3.1 Hot-carrier relaxation/cooling in semiconductors. Source: Nozik (2001b).

In the Shockley–Queisser analysis, a major factor limiting the conversion efficiency to 31% is the loss of the absorbed photon energy above the semiconductor bandgap as heat through electron–phonon scattering and subsequent phonon emission, as the carriers relax to their respective band edges (bottom of the conduction band for electrons and top of the valence band for holes, as shown in Fig. 3.1) and equilibrate with the phonons. The present approach to reduce this loss and increase efficiency above the 31% limit has been to use a stack of cascaded multiple p – n junctions with descending bandgap values along the direction of the incident light such that higher energy photons are absorbed in the higher bandgap semiconductors and lower energy photons in the lower bandgap semiconductors [see Chapter 8 in Vol. I (Yamaguchi, 2001)]; this reduces the overall heat loss due to carrier relaxation via phonon emission. Such cells are generally called tandem solar cells. In the limit of an infinite

stack of bandgaps perfectly matched to the solar spectrum, the ultimate conversion efficiency at 1 Sun intensity increases to about 66%. For practical purposes, the stacks have been limited to two or three p - n junctions; actual efficiencies of about 32% have been reported in laboratory-scale photovoltaic cells with two cascaded p - n junctions, and a world-record 40.7% efficiency has recently been reported with three bandgaps, but with a solar concentration factor of 240 (press release, Spectrolab Inc., 6 Dec. 2006). Although the tandem cell efficiencies are very impressive, their cost is very high, and their main present use is for space applications. However, terrestrial applications using solar concentrators to reduce the net costs are being developed and may lead to competitive PV power costs (McConnell and Symko-Davies, 2006).

Other approaches to exceed the Shockley–Queisser limit have been under investigation for some time. In 1978, it was first proposed that conversion efficiencies above 31% in *single-bandgap* solar cells could be achieved by capturing the excess energy of electron–hole pairs created by the absorption of solar photons with energies larger than the bandgap to do useful work before these high-energy electron–hole pairs convert their excess kinetic energy (equal to the difference between the photogenerated electron energy and the conduction-band energy) to heat through phonon emission (Williams and Nozik, 1978; Boudreaux *et al.*, 1980; Ross and Nozik, 1982; Williams and Nozik, 1984; Nozik, 2001b). Subsequently, additional approaches to high efficiency have been proposed and studied. These approaches have been given the term ‘Third Generation Solar Cells’ by Martin Green (Green, 2001). Besides hot-carrier solar cells (Williams and Nozik, 1978; Boudreaux *et al.*, 1980; Ross and Nozik, 1982; Nozik, 2001b), they include solar cells that produce multiple electron–hole pairs per photon (Kolodinski *et al.*, 1993; Landsberg *et al.*, 1993; Green, 2001; Nozik, 2002; Schaller and Klimov, 2004), multiband and impurity-band solar cells (Luque and Martí, 1997; Green, 2001), thermophotovoltaic/thermophotonic cells (Green, 2001), and up-and-down conversion of the incident solar photons (Trupke *et al.*, 2002a and 2002b). In this chapter, only high-efficiency solar photon conversion approaches will be discussed that are based on the unique properties of nanosize semiconductor particles, interchangeably called nanocrystals (NCs) or quantum dots (QDs). These nanoscale particles exhibit unique and important quantisation effects that arise from the strong quantum confinement of electron and holes in the nanocrystals, which form the basis for several concepts for Third Generation Solar Photon Conversion devices. The diameters of NCs showing strong quantisation effects typically range from 1 nm to 20 nm, depending on the effective masses of the electrons and holes and their Bohr radii in the bulk semiconductor. The strongest confinement and quantisation occurs when the particle radius is less than the Bohr radius.

3.2 Quantisation effects in semiconductor nanostructures

When electrons and holes are confined by potential barriers to small regions of space where the dimensions of the confinement are less than the de Broglie wavelength of these charge carriers, pronounced quantisation effects develop; the length scale below which strong quantisation effects begin to occur ranges from about 5 nm to 25 nm for typical semiconductors (Groups IV, III–V, II–VI). In general, charge carriers in semiconductors can be confined by potential barriers in one, two, or three spatial dimensions. These regimes are termed quantum films, quantum wires, and quantum dots, respectively, and are shown in Fig. 3.2. Only quantum films and quantum dots will be discussed in this chapter.

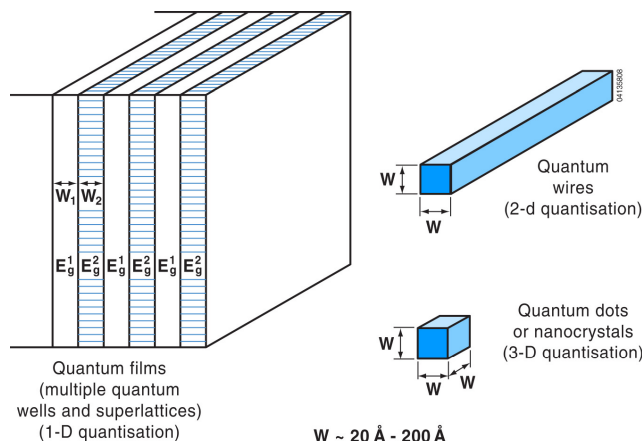


Figure 3.2 Three quantisation configurations depending on whether the confinement is in 1, 2, or 3 dimensions. Source: Nozik and Memming (1996).

Quantum films are more commonly referred to simply as quantum wells (QWs). This is because quantum films were the first quantised semiconductor nanostructures to be extensively studied, beginning in the 1970s (Dingle *et al.*, 1974). These structures were produced by molecular beam epitaxy (MBE) and metallo-organic chemical vapour deposition (MOCVD), and represented textbook examples of a *one-dimensional* quantum well (Dingle, 1987; Bastard, 1988; Jaros, 1989a; Weisbuch and Vinter, 1991; Yoffe, 1993). One-dimensional quantum wells are formed through epitaxial growth of alternating layers of semiconductor materials with different bandgaps. A single quantum well is formed from one semiconductor sandwiched between two layers of a second semiconductor having a larger bandgap; the centre

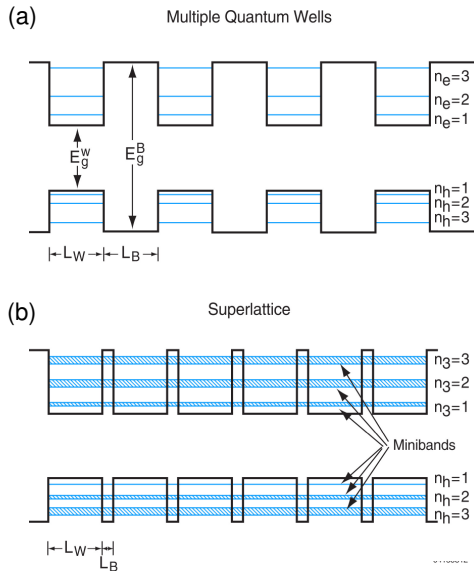


Figure 3.4 Energy levels of (a) multiple quantum wells and (b) superlattices. When the barriers are thick, the wells are isolated, there is no inter-well electronic coupling, and the quantised states are narrow. When the barriers are thin (<4 nm), inter-well electronic coupling occurs, the quantised states broaden, minibands form and electron delocalisation and transport can occur. Source: Nozik and Memming (1996).

Superlattice structures yield efficient charge transport normal to the layers, because the charge carriers can move through the minibands; the narrower the barrier, the wider the miniband and the higher the carrier mobility. Transport in MQWs with thick barriers requires thermionic emission of carriers over the barriers, or if electric fields are applied, field-assisted tunnelling through the barriers (Parsons *et al.*, 1990).

Quantum dots are nanosized semiconductor particles with confinement in all three dimensions. They are most commonly formed in two ways: through colloidal chemistry and via epitaxial deposition from the vapour phase.

3.2.1 Synthesis of semiconductor nanostructures

Quantum wells and superlattices

QWs are produced through epitaxial growth of crystalline films via either MBE or MOCVD. Both techniques are capable of creating epitaxial layers of sufficient quality to produce quantisation effects. These qualities include uniform film thickness and

interfacial abruptness (both within a few atomic layers), crystalline perfection and compositional uniformity.

Molecular beam epitaxy In the MBE technique, an ultrahigh-vacuum chamber is outfitted with a number of evaporation (*i.e.* effusion) cells, each controlled by a separate shutter, which supply fluxes of molecular beams of the desired atomic species. The beams can be turned on and off within 0.1 s. Growth rates are typically 5 Å/s. An ion-beam sputtering gun is used first to ion-etch the surfaces to remove impurities and imperfections. The substrate is maintained at ~500–700 C during growth. Spectroscopic capabilities such as mass spectrometry, Auger spectroscopy, and reflection high-energy electron diffraction are included in the chamber to control the process and provide data on film quality. Elemental species that can be produced by MBE include Ga, Al, In, As, Sb, Sn, Be, Ge, Se, Te, Cd, Hg, Zn, Mn, Pb and Si. The QW materials most commonly produced by MBE are the III–V semiconductor binary and ternary compounds, such as GaAs/Al_xGa_{1-x}As, GaSb/Al_xGa_{1-x}Sb, InAs/GaSb, Ga_xIn_{1-x}As/Al_xIn_{1-x}As, GaAs/Ga_xI_{1-x}P₂ and InP/Ga_xIn_{1-x}As. In each case, the well material is the first, and the barrier material the second, compound. II–VI semiconductor QWs, such as CdTe/HgTe and ZnSe/Zn_{1-x}Mn_xS, have also been made.

Metallo-organic chemical vapour deposition MOCVD is primarily used to prepare III–V semiconductor QWs. In this process the Group III metals are introduced into a reaction chamber in the form of metallo-organic vapours that react at high temperatures with gaseous precursors of the non-metalloid Group V component of the desired semiconductor compound to form a crystalline, epitaxial film on a heated substrate. Ga, Al, and In are commonly introduced as trimethyl gallium (TMG), trimethyl aluminium (TMA) and trimethyl indium (TMI). As and P are usually introduced as arsine and phosphine, although less toxic compounds such as tertiary butyl arsine and tertiary butyl phosphine are also used. The organometallic compounds are kept in liquid form at a sufficiently low, but constant, temperature, and are swept into the reaction chamber at a controlled composition by sparging hydrogen gas at a controlled flow rate through the liquid metallo-organics. Gaseous arsine or phosphine is fed directly into the system from gas cylinders through flow and pressure controllers; ultra-pure hydrogen is used as the carrier gas for all reactant flows. The single-crystal substrate is placed on a graphite block that is heated either by RF or resistance heaters to 650–750 C. Growth rates are typically 5–10 Å/s. The reaction chamber is operated at either atmospheric or reduced pressure (50–100 torr). The low-pressure system can yield very sharp interfaces between the semiconductor heterojunctions and very uniform epilayers, as illustrated in Fig. 3.5.

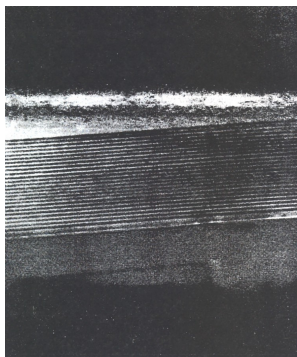


Figure 3.5 TEM of GaAs/Al_{0.32}Ga_{0.68}As superlattice structure. GaAs wells are 52 Å thick and the Al_{0.32}Ga_{0.68}As barriers are 17 Å thick. Source: Nozik (2001b).

Colloidal quantum dots

The most common approach to the synthesis of colloidal QDs is the controlled nucleation and growth of particles in a solution of chemical precursors containing the metal and the anion sources (controlled arrested precipitation) (Overbeek, 1982; Murray, 1995; Weller and Eychmüller, 1997). The technique of forming monodisperse colloids is very old, and can be traced back to the synthesis of gold colloids by Michael Faraday in 1857 (Overbeek, 1982; Murray, 1995). A common method for II–VI colloidal QD formation is to rapidly inject a solution of chemical reagents containing the Group II and Group VI species into a hot and vigorously stirred solvent containing molecules that can coordinate with the surface of the precipitated QD particles (Murray *et al.*, 1993; Murray, 1995; Weller and Eychmüller, 1997). A large number of nucleation centres are initially formed, and the coordinating ligands in the hot solvent prevent or limit particle growth via the normal process of Ostwald ripening (*i.e.* the growth of larger particles at the expense of smaller particles to minimise the higher surface free energy associated with smaller particles). Further improvement of the resulting size distribution of the QD particles can be achieved through size-selective precipitation (Murray *et al.*, 1993; Murray, 1995), whereby slow addition of a non-solvent to the colloidal solution of particles causes precipitation of the larger particles (the solubility of molecules with the same type of chemical structure decreases with increasing size). This process can be repeated several times to narrow the size distribution of II–VI colloidal QDs to a few percent of the mean diameter.

The synthesis of colloidal III–V QDs is more difficult than for II–VI QDs. Because the synthesis must be conducted in rigorously air-free and water-free atmospheres, it generally requires higher reaction temperatures and much longer reaction times, and it involves more complicated organometallic chemistry. For example, for the synthesis of InP QDs (Mičić *et al.*, 1994, 1995, 1996 and 1997; Guzelian *et al.*, 1996b; Banin *et al.*, 1997) an indium salt [$\text{In}(\text{C}_2\text{O}_4)_3$, InF_3 , or InCl_3] is reacted with trimethylsilylphosphine [$\text{P}(\text{Si}(\text{CH}_3)_3)_3$] in a solution of trioctylphosphine oxide (TOPO) and trioctylphosphine (TOP) to form a soluble InP organometallic precursor species that contains In and P in a 1:1 ratio. The InP precursor species in the TOPO/TOP solution is then heated for several days at a temperature ranging from 270 C to 290 C, depending on the desired QD properties. One difference with the synthesis of II–VI materials is that more than one day of heating at reaction temperature is required to form crystalline III–V QDs, whereas II–VI QDs form immediately on injection of the reactants into the hot TOPO/TOP solution.

The resulting InP QDs contain a capping layer of TOPO, which can be readily exchanged for several other types of capping agents, such as thiols, pyridines, amines and polymers. The size distribution of the InP QDs can be further narrowed to less than 10% through selective precipitation techniques. Finally, they can be studied in the form of colloidal solutions, powders, or dispersed in transparent polymers or organic glasses (for low-temperature studies); capped InP QDs recovered as powders can also be redissolved to form transparent colloidal solutions.

In addition to InP QDs, similar methods have been used to produce III–V QDs of GaP (Mičić *et al.*, 1995; Mičić and Nozik, 1996), GaInP_2 (Mičić *et al.*, 1995; Mičić and Nozik, 1996), GaAs (Olshavsky *et al.*, 1990; Uchida *et al.*, 1992; Nozik *et al.*, 1993; Mičić *et al.*, 1995; Mičić and Nozik, 1996), and InAs (Guzelian *et al.*, 1996a); higher temperatures (400 C) are required for GaP and GaInP_2 QDs.

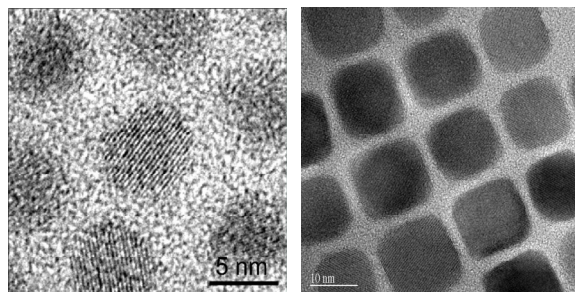


Figure 3.6 Transmission electron micrograph of PbSe QD spheres (5 nm dia) and cubes (10 nm). The spherical QD dots contain about 20 rows of atoms, or ~6000 atoms.

Group IV–VI QDs can also be readily formed and the size and shape easily controlled [(Murphy *et al.*, 2006) and references therein]. Figure 3.6 shows TEM images of PbSe QD spheres and cubes.

Stranski–Krastanov epitaxial growth

QDs can also be produced via epitaxial growth from the vapour phase on appropriate substrates; the growth can be effected using either MBE or MOCVD. In the Stranski–Krastanov (SK) mode of QD formation, a thin semiconductor film is deposited by MBE or MOCVD onto another semiconductor substrate material that has a mismatch in lattice constant with the material being deposited. If the lattice mismatch is sufficiently high and the film has a higher surface energy than the substrate, then after the initial growth of a few monolayers (called the wetting layer), subsequent deposition forms small islands which are in the QD size regime. The size, shape, perfection and density of these SK QDs can be controlled by controlling the conditions in the MBE or MOCVD reactor. The bulk of work on these SK QDs has been on $\text{InGa}_x\text{As}_{1-x}$ QDs grown on GaAs substrates (Sugawara, 1999); InP QDs grown on GaAs or $\text{Al}_x\text{Ga}_{1-x}\text{As}$ substrates have also been reported (Hanna *et al.*, 1997). The size of SK QDs is generally larger than that of colloidal QDs; they typically have a lateral dimension of 1000–2000 Å and a height of 100–500 Å. For III–V semiconductors these sizes produce quantisation effects because their Bohr radius is large, but the degree of quantisation is not as strong as that in colloidal QDs where the sizes range from 15 Å to 100 Å. The shape of the InAs/GaAs SK QDs has been reported to be a square-based pyramid (Ruminov and Scheerschmidt, 1995); however, other results suggest a parallelogram base and C_{2v} symmetry (Lee *et al.*, 1998; Yang *et al.*, 2000).

Another configuration of SK type QDs is possible. In this case, a QW which has a thin outer barrier (about 100 Å) is first formed. SK islands of another semiconductor material having a lattice mismatch with the barrier are then deposited on top of the barrier. These SK islands produce a parabolic strain field which propagates down through the barrier into the QW. In the case of InP SK islands (called stressor islands) formed on an AlGaAs/GaAs/AlGaAs QW, the strain field expands the GaAs lattice and reduces the GaAs bandgap just below the InP islands (Hanna *et al.*, 1997). Thus, the GaAs QW beneath the InP stressor islands is converted into a QD since the one-dimensional confinement of carriers is transformed into three-dimensional confinement. An important feature of this type of QD is that both the well and barrier region of the QD are made of the same material. This eliminates interface defects and interface states that complicate the relaxation behaviour of photogenerated carriers.

3.2.2 Energy levels in quantum wells, superlattices and quantum dots

Quantum wells and superlattices

The confinement of electrons or holes in potential wells leads to the creation of discrete energy levels in the wells, compared with the continuum of states in bulk material; quantisation also leads to a major change in the density of states. The energy levels can be calculated by solving the Schrödinger equation for the well-known particle in a box problem. Using the effective mass envelope function approximation (Bastard, 1981 and 1982; Altarelli, 1985; Bastard and Brum, 1986), the electron wavefunction ψ_n is then

$$\psi_n = \sum_{W,B} e^{ik \cdot r} U_k^{W,B}(r) \phi_n(z) \quad (3.3)$$

where W and B refer to well and barrier, respectively; k is the transverse electron wave vector; z is the growth direction; $U_k^{W,B}(r)$ is the Bloch wavefunction in W or B ; and $\phi_n(z)$ is the envelope wavefunction. The envelope wavefunction is determined by solving the Schrödinger equation

$$\left(\frac{\hbar^2}{2m^*} \frac{\partial^2}{\partial z^2} + V_c(z) \right) \phi_n(z) = E_n \phi_n(z) \quad (3.4)$$

where $V_c(z)$ is the potential barrier function, and E_n the quantised energy level in the well.

Considering first isolated QWs that are infinitely deep, the solution to eq. 3.4 becomes very simple since the wavefunctions must be zero at the well-barrier interfaces. This leads to the well-known solutions

$$\psi_n = A \sin \frac{n\pi z}{L_w} \quad (3.5)$$

$$E_n = \frac{\hbar^2}{2m^*} \left(\frac{n\pi}{L_w} \right)^2, \quad n=1, 2, 3, \dots \quad (3.6)$$

where L_w is the well width.

For the more realistic case of finite barrier heights, eq. 3.4 cannot be solved exactly, but requires either a graphical or numerical solution. For the case where the effective masses in the well and barrier are taken to be equal

$$\phi_n(z) = A \cos kz \text{ (inside well)} \quad (3.7)$$

$$\phi_n(z) = B \exp[-k(z - L_w/2)] \text{ (outside well)} \quad (3.8)$$

where

$$E_n = \frac{\hbar^2 k^2}{2m^*} - V_o, \quad -V_o < E_n < 0 \quad (3.9)$$

and

$$\cos(kL_w/2) = k/k_o \text{ for } \tan kL_w/2 > 0 \quad (3.10)$$

$$\sin(kL_w/2) = k/k_o \text{ for } \tan kL_w/2 > 0 \quad (3.11)$$

where

$$k_2 = 2m^* V_o / \hbar^2 \quad (3.12)$$

and V_o is the barrier height.

There is always at least one state in the well no matter how thin it is; the number of bound states is given by

$$1 + \text{Int} \left[\frac{(2m^* V_o L_w^2)^{1/2}}{\pi^2 \hbar^2} \right] \quad (3.13)$$

where $\text{Int}[x]$ indicates the integer part of the argument.

The calculation of the hole levels is much more complicated since the band structure of many important semiconductors has hole bands with fourfold degeneracy at $k=0$. This leads to heavy and light holes with different effective masses. Consequently, a double set of hole energy levels is formed in the QW with different spacings between levels—one set for the light holes, the second set for the heavy holes, as shown in Fig. 3.3. Solutions to the problem have been reported for both infinite (Bastard, 1981; Altarelli, 1985) and finite (Bastard and Brum, 1986) potential barriers.

For superlattices, several approaches have been used to calculate the energy level structure of the minibands (Bastard, 1981; Altarelli, 1985; Bastard and Brum, 1986). One approach is to use a tight-binding model for the multiple wells, leading to a Bloch-like envelope function of the form (Dingle *et al.*, 1975)

$$\psi_q^i(z) = \frac{1}{\sqrt{N}} \sum_n e^{ipnx} \phi^i(z - nx) \quad (3.14)$$

where $\Psi^i(z - nx)$ is the i th wavefunction of the QW and q is the Bloch wave vector.

This approach leads to results that are summarised in Fig. 18, Chapter 1 of Dingle (1987), which shows the energy levels as a function of barrier thickness. That figure shows the formation of minibands with energy bandwidths that increase rapidly with decreasing barrier widths below 40 Å.

The density of states (DOS) also shows profound changes with the dimensionality of quantisation. For ideal bulk semiconductors with simple parabolic energy bands, the DOS has a square-root dependence on electron energy

$$N(E)_{\text{bulk}} = \sqrt{2}(m^*)^{3/2} \pi^2 \hbar^{-3} E^{1/2} \quad (3.15)$$

For an ideal QW, the DOS shows a step-like function with each plateau having a DOS of

$$N(E)_{\text{QW}} = nm^* / \pi \hbar^2 \quad (3.16)$$

where n is the quantum number of the state.

For a superlattice, the steepness of the steps is destroyed by the dispersion of the N states in a miniband (Dingle, 1987; Weisbuch and Vinter, 1991)

$$N(E)_{\text{SL}} = N \frac{m^*}{\pi \hbar^2} \arccos \left(\frac{\varepsilon_i - E_i - S_i}{2 x_i} \right) \quad (3.17)$$

where ε_i is the energy dispersion caused by superlattice formation and the i th quantum state, E_i is the energy of the i th quantum state for the isolated quantum well, S_i is the electron transfer matrix describing transmission through the potential barrier from the i th quantum state, and x_i is the square root of the electron transmission probability at the i th quantum state.

Figure 3.7 shows these DOS functions for bulk semiconductors, QWs, superlattices, quantum wires and quantum dots; the DOS for quantum dots exhibits discrete values at the discrete quantised energy levels.

Quantum dots

The earliest and simplest treatment of the electronic states of a QD is based on the effective mass approximation (EMA); the simple EMA treatment can be improved by incorporating the $\mathbf{k} \cdot \mathbf{p}$ approach, which has commonly been used to calculate the electronic structure of bulk semiconductor and QW structures.

The EMA rests on the assumption that if the QD is larger than the lattice constants of the crystal structure, then it will retain the lattice properties of the infinite crystal and the same values of the carrier effective masses; the electronic properties of the

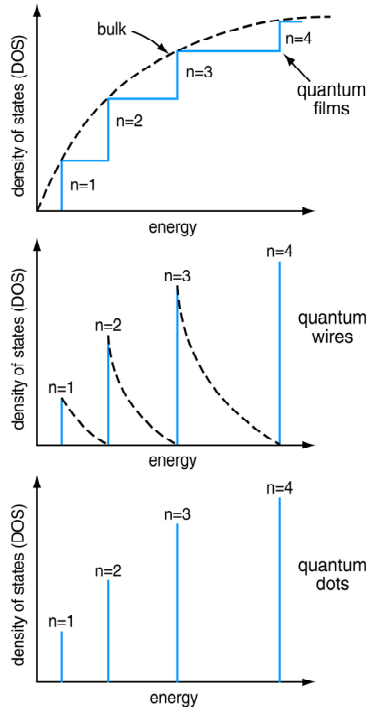


Figure 3.7 Density of states for bulk semiconductors, quantum films, quantum wires and quantum dots.

Source: Nozik and Memming (1996).

QD can then be determined by simply considering the modification of the energy of the charge carriers produced by the quantum confinement. Thus, the electronic properties are determined by solving the Schrödinger equation for a particle in a 3-dimensional box. The zeroth order approximation is a perfectly spherical QD with infinite potential walls at the surface. Strong confinement is defined as the case where the QD size is small compared with the de Broglie wavelength of electrons in the box or small compared with the Bohr radius of the bound electron–hole pair (exciton) in the bulk; this is the case for II–VI and III–V semiconductors. Taking into account the Coulomb interaction between electrons and holes, which is enhanced due to confinement in the QD, the Hamiltonian can then be written

$$\hat{H} = -\frac{\hbar^2 \nabla_e^2}{2m_e^*} - \frac{\hbar^2 \nabla_h^2}{2m_h^*} - \frac{q^2}{\epsilon |r_e - r_h|} + V_e(r_e) + V_h(r_h) \quad (3.18)$$

and

$$\hat{H}\psi(r) = E\psi(r) \quad (3.19)$$

where V_e and V_h are the confining potentials, r_e and r_h are the distances of the electron and hole from the centre of the QD, and ϵ is the permittivity of the semiconductor.

Analytical solutions of eqs. 3.18 and 3.19 are difficult because centre-of-mass motion and reduced mass motion cannot be separated as independent coordinates. Various approaches to solving this problem have been used. These include perturbation theory (Brus, 1984 and 1986), variational calculations (Schmidt and Weller, 1986; Kayanuma, 1988; Ekimov *et al.*, 1989; Kayanuma and Momiji, 1990; Takagahara, 1993a and 1993b; Kagan, 1996, p. 287), matrix diagonalisation (Hu *et al.*, 1990; Park *et al.*, 1990), and Monte Carlo methods (Pollock and Koch, 1991). Perturbation theory (Brus, 1984 and 1986) and variational calculations (Kayanuma, 1988) lead to a solution of the form

$$E_{\min} = \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8q^2}{\epsilon_s R} - 0.25E_{\text{Ryd}}^* \quad (3.20)$$

where $E_{\min}$ is the lowest energy separation between hole and electron states in the QD, E_{Ryd}^* is the bulk exciton binding energy in meV, and R is the QD radius. $E_{\min}$ is often referred to as the bandgap of the QD since it represents the threshold energy for photon absorption, blue-shifted from the bulk bandgap, E_g .

Improvements in the EMA model involve accounting for band non-parabolicity and hole-state mixing (Grigoryan *et al.*, 1990; Sercel and Vahala, 1990; Nomura and Kobayashi, 1991; Efros, 1992; Koch *et al.*, 1992; Ekimov *et al.*, 1993), finite barrier heights (Kayanuma and Momiji, 1990), and surface polarisation (Banyai *et al.*, 1992).

In the effective mass $\mathbf{k} \bullet \mathbf{p}$ approach, the QD wavefunctions are expanded as a linear combination of N_b bulk Bloch functions at the $\mathbf{k} = 0$ Brillouin zone centre (Γ point) (Grigoryan *et al.*, 1990; Sercel and Vahala, 1990); for these calculations, values of N_b up to 8 (termed the 8-band $\mathbf{k} \bullet \mathbf{p}$ model) have been used (Banin *et al.*, 1998). The effective mass $\mathbf{k} \bullet \mathbf{p}$ approach has been very extensively used for QDs, but its rigour has been debated (Fu *et al.*, 1997, 1998a and 1998b; Efros and Rosen, 1998 and 2000). An approach based on direct diagonalisation and pseudopotentials is proposed as a better theoretical basis on which to calculate the electronic states in QDs (Fu *et al.*, 1997 and 1998a). A comparison of the calculated electron and hole states for a 28 Å InP QD using a 6-band $\mathbf{k} \bullet \mathbf{p}$ model (Fu and Zunger, 1998) and the direct diagonalisation pseudopotential model (Fu and Zunger, 1998) indicates a higher density of electronic states for the latter than the former.

Because of the three-dimensional spatial confinement in QDs, the solution of the Schrödinger equation results in describing the electronic states in the QD by three quantum numbers plus spin. A commonly used notation (Woggon, 1997; Xia, 1989) labels the electron states as nL_e and the hole states as nL_F , where n is the principal quantum number (1,2,3 *etc.*), L is the orbital angular momentum (S, P, D *etc.*), and F is the total angular momentum ($F = L + J$, and $J = L + S$), where S is the spin, and the projection of F along a magnetic axis is $m_F = -F$ to $+F$. Thus electron states become $1S_e$, $2S_e$, $1P_e$ *etc.*, and hole states become $1S_{1/2}$, $1S_{3/2}$, $1P_{1/2}$ *etc.* For optical transitions in ideal spherical QDs, the selection rules are $\Delta n = 0$, $\Delta L = 0, \pm 2$; and $\Delta F = 0, \pm 1$. These rules can be broken by non-spherical QDs and strong hole-state mixing.

3.3 Optical spectroscopy of quantum wells, superlattices and quantum dots

3.3.1 Quantum wells and superlattices

Optical transitions between quantum levels can occur on excitation with light. The interband transition probability is the product of an optical matrix element (M) times a DOS term. M involves the electric dipole operator and can be expressed as (Weisbuch and Vinter, 1991)

$$M = \left\langle \phi_e(z) e^{ik_e \cdot r} u_{cke}(r) \middle| \hat{\mathbf{n}} \middle| \phi_h(z) e^{ik_h \cdot r} u_{vkh}(r) \right\rangle \quad (3.21)$$

where $\phi_e(z)$ and $\phi_h(z)$ are the electron and hole envelope wavefunctions, k_e and k_h are electron and hole wave vectors, $\hat{\mathbf{n}}$ is the polarisation vector of the light, and $u_{cke}(r)$ and $u_{vkh}(r)$ are the Bloch functions. The integration of eq. 3.21 produces a factor $[\phi_e(z)\phi_h(z)]$ which becomes unity for transitions between electron and hole states with the same quantum number. Thus the selection rule for optical interband transitions is that $\Delta n = 0$. Some additional factors affecting optical transitions are: (a) heavy hole–electron transitions are expected to be three times stronger than light hole–electron transitions; (b) transitions involving different n values become possible in the presence of an electric field and also when finite wells are considered; (c) parity is a good quantum number, and transitions involving the same parity are allowed.

In light of the above discussion, the optical absorption spectrum of a quantum film is expected to consist of a series of steps, with the position of these steps corresponding to the transitions between heavy or light hole quantum states and electron quantum states following the selection rule $\Delta n = 0$. Furthermore, since the widths of the wells are commonly smaller than the calculated diameter of an exciton, the exciton binding

energy is greatly increased in QWs, and the excitons can be stable even at room temperature. Thus the absorption spectra of QWs can be expected to show exciton peaks, even at room temperature, which occur at energies below the step. Such spectra have indeed been observed by many workers (Dingle *et al.*, 1974 and 1975).

3.3.2 Quantum dots

The optical absorption and emission properties of quantum dots follow the same general photophysics as QWs and SLs in that the probability for dipole-allowed optical transitions is proportional to the matrix element connecting the initial [$\psi_i(r)$] and final [$\psi_f(r)$] states through the dipole operator ($\hat{\mathbf{n}}$)

$$M_{\text{QD}} = \langle \psi_f(r) | \hat{\mathbf{n}} | \psi_i(r) \rangle \quad (3.22)$$

The wavefunctions for three-dimensional confinement have three quantum numbers (n, l, m) plus spin. The selection rules for dipole-allowed absorption and emission were given above for interband transitions. For intraband transitions between the ladder of electron or hole states, the selection rules for the simplest case of non-interacting electrons and holes are $\Delta n \neq 0$; $\Delta L = 0, \pm 1$; $\Delta m = 0, \pm 1$.

As an example, Fig. 3.8 shows the absorption and emission spectra of initially prepared InP QDs with a mean diameter of 32 Å. Samples were prepared by dispersing washed QDs in toluene, and optical absorption and photoluminescence spectra collected at room temperature. Other III–V and II–VI QDs exhibit similar behaviour. The absorption spectrum shows an excitonic peak at about 590 nm. The photoluminescence (PL) spectrum (excitation at 500 nm) shows two emission bands: a weaker one near the band edge with a peak at 655 nm, and a second, stronger, broader band that peaks above 850 nm. The PL band with deep red-shifted subgap-emission peaking above 850 nm is attributed to radiative recombination in QD surface states produced by phosphorus vacancies (Mićić *et al.*, 1996). These surface defects and the accompanying red-shifted emission can be completely removed by etching the InP QDs with HF; intense band-edge emission from the QDs can then be observed. After etching, the PL intensity increases by a factor of ten, and the near-infrared emission produced by the deep surface traps is completely removed (Mićić *et al.*, 1996). The near-band-edge quantum yield (QY) increases from 30% to 60% as the temperature decreases from 300 K to 10 K (Mićić *et al.*, 1996) (see Fig. 3.9).

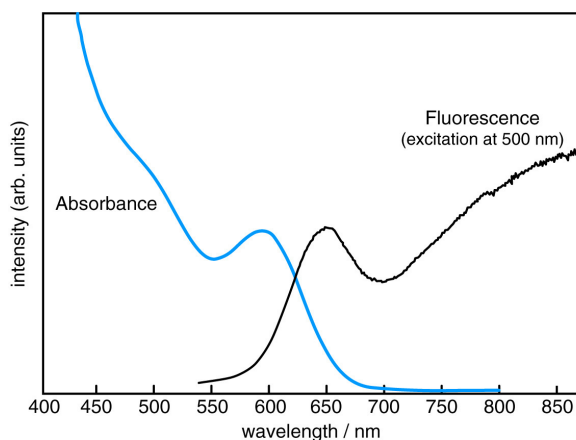


Figure 3.8 Absorption and emission spectra at 300 K for InP QD with excess In^{3+} (In:P = 1.6:1).

Source: Mičić *et al.* (1996).

The absorption spectrum in Fig. 3.8 shows an excitonic peak at about 590 nm. The photoluminescence (PL) spectrum (excitation at 500 nm) shows two emission bands: a weaker one near the band edge with a peak at 655 nm, and a second, stronger, broader band that peaks above 850 nm. The PL band with deep red-shifted subgap-emission peaking above 850 nm is attributed to radiative recombination in QD surface states produced by phosphorus vacancies (Mičić *et al.*, 1996). These surface defects and the accompanying red-shifted emission can be completely removed by etching the InP QDs with HF; intense band-edge emission from the QDs can then be observed. After etching, the PL intensity increases by a factor of ten, and the near-infrared emission produced by the deep surface traps is completely removed (Mičić *et al.*, 1996). The near-band-edge quantum yield (QY) increases from 30% to 60% as the temperature decreases from 300 K to 10 K (Mičić *et al.*, 1996) (see Fig. 3.9).

Figure 3.9 shows the room-temperature absorption spectra as a function of QD size ranging from 26 Å to 60 Å, measured by transmission electron microscopy (TEM) (Mičić *et al.*, 1997). The absorption spectra show one or more broad excitonic peaks which reflect substantial inhomogeneous line broadening arising from the QD size distribution; as expected, the spectra shift to higher energy as the QD size decreases (Mičić *et al.*, 1997). The colour of the InP QD samples changes from deep red (1.7 eV) to green (2.4 eV) as the diameter decreases from 60 Å to 26 Å. Bulk InP is black with a room-temperature bandgap of 1.35 eV and an absorption onset at 918 nm. Higher energy transitions above the first excitonic peak in the absorption spectra can also be easily seen in QD samples with mean diameters equal to or greater

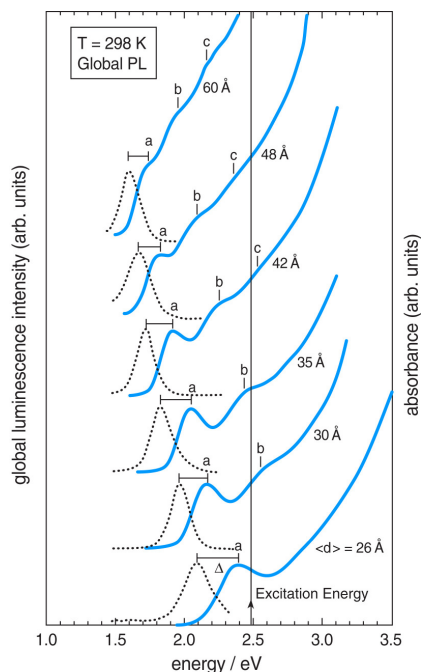


Figure 3.9 Absorption (solid line) and global photoluminescence (dotted line) spectra at 298 K for colloidal ensembles of InP quantum dots with different mean diameters. All samples were photoexcited at 2.48 eV. Source: Mičić *et al.* (1997).

than 30 Å. The spread in QD diameters is generally about 10% and is somewhat narrower in samples with larger mean diameters; this is why higher energy transitions can be resolved for the larger-sized QD ensembles. All of the prepared QD nanocrystallites are in the strong confinement regime since the Bohr radius of bulk InP is ~ 100 Å. Figure 3.9 shows typical room-temperature absorption and global emission spectra of InP colloids with mean particle diameters ranging from 26 Å to 60 Å as measured by TEM (Mičić *et al.*, 1997); the excitation energy for all the QD sample ensembles in Fig. 3.9 was 2.48 eV, well above their absorption onset in each case.

The global emission peaks in Fig. 3.9 show an increasing red shift from the first excitonic absorption peak as the mean QD size decreases from 60 Å to 26 Å. The global ('nonresonant') red shift is as large as 300 meV for samples with the smallest mean diameter (Mičić *et al.*, 1997). Global PL is defined as that observed when the excitation energy is much higher than the energy of the absorption threshold exhibited in the absorption spectrum produced by the ensemble of QDs in the sample; thus a large fraction of all the QDs in the sample is excited. The resulting global PL shows a

very broad peak (line width of 175–225 meV) that is red-shifted by 100–300 meV from the first absorption peak. The broad PL line width is caused by inhomogeneous line broadening arising from the ~10% size distribution sampled in the global PL experiment. The large global red shift is caused by the volume dominance of the larger particles in the size distribution; the latter will absorb most of the incident photons and will show large red shifts since the PL excitation energy is well above their lowest transition energy.

3.4 Hot electron and hole cooling dynamics in quantum-confined semiconductors

As indicated in Section 3.1, the maximum solar photon conversion efficiency for a single-gap absorber is limited to 31% if the photogenerated hot electrons and holes created with energies above the conduction and valence bands convert their initial excess kinetic energy into heat through phonon emission. If the hot electrons and holes can convert their excess energy into electrical or chemical free energy instead of heat, then the ultimate thermodynamic efficiency can be increased to 66% (Ross and Nozik, 1982). To do this, the rate of conversion to useful free energy must be faster than the rate of cooling via phonon emission. It is therefore important to determine and understand the dynamics of hot electron and hole cooling, and how these dynamics can be modified and controlled in quantum-confined structures; this is the subject of this section.

3.4.1 Quantum wells and superlattices

In this section we will discuss the electron and hole cooling dynamics in III–V QWs and SLs compared with bulk III–V semiconductors. These dynamics can be determined from several types of time-resolved PL experiments. One technique involves hot luminescence non-linear correlation (Xu and Tang, 1984; Rosker *et al.*, 1986; Edelstein *et al.*, 1987), which is a symmetrised pump–probe type of experiment. Figure 2 of Edelstein *et al.* (1987) compares the hot-electron relaxation times as a function of the electron energy level in the well for bulk GaAs and a 20-period MQW of GaAs/Al_{0.38}Ga_{0.62}As containing 250 Å GaAs wells and 250 Å Al_{0.38}Ga_{0.62}As barriers. For bulk GaAs, the hot-electron relaxation time varies from about 5 ps near the top of the well to 35 ps near the bottom of the well. For the MQW, the corresponding hot-electron relaxation times are 40 ps and 350 ps.

Another method uses time-correlated single-photon counting to measure PL lifetimes of hot electrons. Figure 3.10 shows three-dimensional plots of PL intensity as a function of energy and time for both bulk GaAs and a 250 Å/250 Å GaAs/Al_{0.38}Ga_{0.62}As MQW (Rosenwaks *et al.*, 1993). It is clear from these plots that the MQW sample exhibits much longer-lived hot luminescence (*i.e.* luminescence above the lowest $n = 1$ electron to heavy-hole transition at 1.565 eV) than bulk GaAs. Depending on the emitted photon energy, the hot PL for the MQW is seen to exist beyond times ranging from hundreds to several thousand picoseconds. On the other hand, the hot PL intensity above the bandgap (1.514 eV) for bulk GaAs is negligible over most of the plot; it is only seen at the very earliest times and at relatively low photon energies.

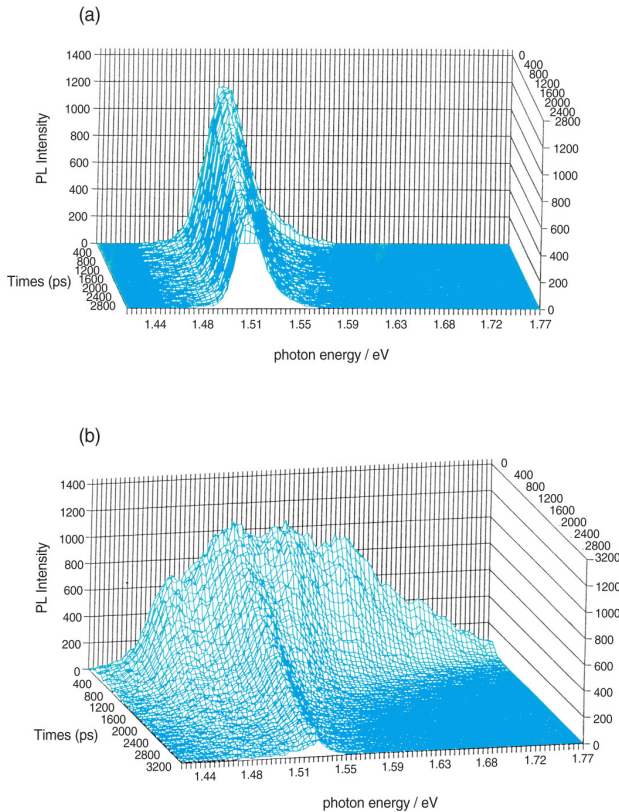


Figure 3.10 Three-dimensional plots of photoluminescence intensity *versus* time and photon energy for (a) bulk GaAs and (b) 250 Å GaAs/250 Å Al_{0.38}Ga_{0.62}As MQW. Source: Rosenwaks *et al.* (1993).

Rosenwaks *et al.* (1993) performed calculations on the PL intensity *versus* time and energy data to determine the time dependence of the quasi-Fermi level, electron temperature, electronic specific heat, and ultimately the dependence of the characteristic hot-electron cooling time on electron temperature.

The cooling, or energy-loss, rate for hot electrons is determined by LO phonon emission through electron–LO-phonon interactions. The time constant characterising this process can be described by the following expression (Ryan *et al.*, 1984; Cai *et al.*, 1986; Christen and Bimberg, 1990)

$$P_e = -\frac{dE}{dt} = \frac{\hbar\omega_{LO}}{\tau_{avg}} \exp(-\hbar\omega_{LO}/kT_e) \quad (3.23)$$

where P_e is the power loss of electrons (*i.e.* the energy-loss rate), $\hbar\omega_{LO}$ is the LO phonon energy (36 meV in GaAs), T_e is the electron temperature, and τ_{avg} is the time constant characterising the energy-loss rate.

The electron energy-loss rate is related to the electron-temperature decay rate through the electronic specific heat. Since the electron distribution becomes degenerate at high light irradiance, the classical specific heat is no longer valid. Hence the temperature- and density-dependent specific heat for both the QW and bulk samples need to be calculated as a function of time in each experiment so that τ_{avg} can be determined.

The results of such calculations, presented in Fig. 2 of Rosenwaks *et al.* (1993), show a plot of τ_{avg} *versus* electron temperature for bulk and MQW GaAs at high and low carrier densities. At a high carrier density [$n \sim (2-4) \times 10^{18} \text{ cm}^{-3}$], the τ_{avg} values for the MQW are much higher ($\tau_{avg} = 350-550 \text{ ps}$ for T_e between 440 K and 400 K) compared with bulk GaAs ($\tau_{avg} = 10-15 \text{ ps}$ over the same T_e interval). On the other hand, at a low carrier density [$n \sim (3-5) \times 10^{17} \text{ cm}^{-3}$] the differences between the τ_{avg} values for bulk and MQW GaAs are much smaller.

A third technique to measure cooling dynamics is PL upconversion. For example, Rosenwaks *et al.* (1993) recorded time-resolved luminescence spectra at room temperature for a 4000-Å bulk GaAs sample at incident pump powers of 25, 12.5 and 5 mW. They determined electron temperatures by fitting the high-energy tails of the spectra, choosing only the region which is linear on a semilogarithmic plot for the fit. The carrier densities for the sample were 1×10^{19} , 5×10^{18} , and $2 \times 10^{18} \text{ cm}^{-3}$, corresponding to the incident excitation powers of 25, 12.5 and 5 mW, respectively. Spectra for the MQW sample were recorded at the same pump powers as the bulk. Figure 3.11 shows τ_{avg} for bulk and MQW GaAs at the three irradiances, again showing the much slower cooling in MQWs (by up to two orders of magnitude).

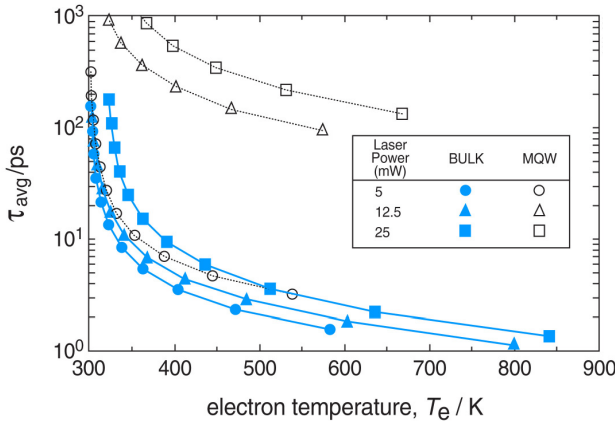


Figure 3.11 Time constant for hot-electron cooling (τ_{avg}) versus electron temperature for bulk GaAs and GaAs multiple quantum wells at three excitation intensities. Source: Rosenwaks *et al.* (1993).

The difference in hot-electron relaxation rates between bulk and quantised GaAs structures is also reflected in time-integrated PL spectra. Typical results are presented [see Fig. 7 in Nozik (2001b)] for single-photon counting data taken with 13 ps pulses of 600 nm light at 800 kHz focussed to about 100 μm with an average power of 25 mW (Nozik *et al.*, 1990). The time-averaged electron temperatures obtained from fitting the tails of these PL spectra to the Boltzmann function show that the electron temperature varies from 860 K for the 250 Å/250 Å MQW to 650 K for the 250 Å/17 Å superlattice, while bulk GaAs has an electron temperature of 94 K, which is close to the lattice temperature (77 K). The variation in the electron temperatures between the quantised structures can be attributed to differences in electron delocalisation between MQWs and SLs, and the associated non-radiative quenching of hot-electron emission.

As shown above, the hot-carrier cooling rates depend on photogenerated carrier density; the higher the electron density, the slower the cooling rate. This effect is also found for bulk GaAs, but it is much weaker than in quantised GaAs. The most generally accepted mechanism for the decreased cooling rates in GaAs QWs is an enhanced hot phonon bottleneck (Lugli and Goodnick, 1987; Joshi and Ferry, 1989; Campos *et al.*, 1992). In this mechanism, a large population of hot carriers produces a non-equilibrium distribution of phonons (in particular, optical phonons, which are the type involved in the electron–phonon interactions at high carrier energies), because the optical phonons cannot equilibrate fast enough with the crystal bath; these hot phonons can be reabsorbed by the electron plasma to keep it hot (see Fig. 3.12). In

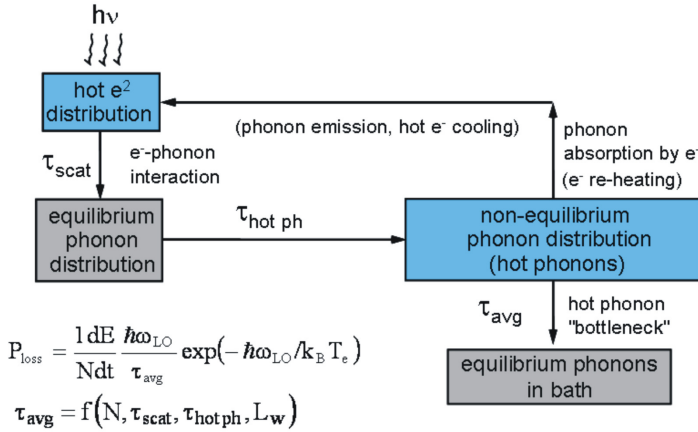


Figure 3.12 Hot phonon bottleneck to slow hot-electron cooling in QWs. At high light intensity, hot electrons produce hot phonons which can reheat electrons via phonon absorption to keep them hot. P_{loss} is power loss per electron.

QWs, the phonons are confined in the well and they exhibit slab modes (Campos *et al.*, 1992), which enhance the hot phonon bottleneck effect.

The first prediction of slowed cooling at low light intensities in quantised structures was made by Boudreaux, Williams, and Nozik (Boudreaux *et al.*, 1980). They anticipated that cooling of carriers would require multiphonon processes when the quantised levels are separated in energy by more than phonon energies. They analysed the expected slowed cooling time for hot holes at the surface of highly doped *n*-type TiO_2 semiconductors, where quantised energy levels arise because of the narrow space-charge layer (*i.e.* depletion layer) produced by the high doping level. The carrier confinement in this case is produced by the band bending at the surface; for a doping level of $1 \times 10^{19} \text{ cm}^{-3}$, the potential well can be approximated as a triangular well extending 200 Å from the semiconductor bulk to the surface and with a depth of 1 eV at the surface barrier. The multiphonon relaxation time was estimated from the approximation

$$\tau_c \sim \omega^{-1} \exp(\Delta E / kT) \quad (3.24)$$

where τ_c is the hot-carrier cooling time, ω is the phonon frequency, and ΔE is the energy separation between quantised levels. For strongly quantised electron levels, with $\Delta E > 0.2 \text{ eV}$, τ_c could be $> 100 \text{ ps}$ according to eq. 3.24.

However, carriers in the space-charge layer at the surface of a heavily doped semiconductor are only confined in one dimension, as in a quantum film. This

quantisation regime leads to discrete energy states which have dispersion in $\mathbf{k}$ -space (Jaros, 1989b). This means the hot carriers can cool by undergoing interstate transitions which require only one emitted phonon followed by a cascade of single phonon intrastate transitions; the bottom of each quantum state is reached by intrastate relaxation before an interstate transition occurs. Thus the simultaneous and slow multiphonon relaxation pathway can be bypassed by single-phonon events, and the cooling rate increases correspondingly.

3.4.2 Quantum dots

As previously discussed, slowed hot-electron cooling in QWs and SLs that is produced by a *hot* phonon bottleneck requires very high light intensities in order to create the required photogenerated carrier density of greater than about $1 \times 10^{18} \text{ cm}^{-3}$. This required intensity, possible with laser excitation, is many orders of magnitude greater than that provided by solar radiation at the Earth's surface (the maximum solar photon flux is about $10^{18} \text{ cm}^{-2} \text{ s}^{-1}$; assuming a carrier lifetime of 1 ns and an absorption coefficient of $1 \times 10^5 \text{ cm}^{-1}$, this translates into a photoinduced electron density of about 10^{14} cm^{-3} at steady state). Hence it is not possible to obtain slowed hot-carrier cooling in semiconductor QWs and superlattices with unconcentrated solar irradiation via a *hot* phonon bottleneck effect; solar concentration ratios greater than 10^4 would be required, resulting in severe practical problems.

However, the situation with three-dimensional confinement in quantum dots is more favourable. In the QD case, slowed hot-electron cooling is theoretically possible, even at arbitrarily low light intensity; this effect is simply called a phonon bottleneck, without the qualification of requiring hot phonons (*i.e.* a non-equilibrium distribution of phonons). More rigorous theoretical models for slowed cooling in quantised nanoparticles have been proposed by Bockelmann and coworkers (Bockelmann and Bastard, 1990; Bockelmann and Egeler, 1992) and Benisty and coworkers (Benisty, 1991; Benisty *et al.*, 1995). Thus, the slowed cooling could make the rate of other useful paths for the relaxation of highly energetic electron-hole pairs (*i.e.* excitons) competitive with cooling. One such important process is the creation of additional excitons in QDs when the absorbed photon energy is greater than twice the QD bandgap (HOMO-LUMO or $1S_h-1S_e$ transition). This process is known in bulk semiconductors as impact ionisation and is an inverse process to an Auger process, whereby one of two electron-hole pairs recombines non-radiatively and transfers this energy to the remaining electron or hole to create an excited electron-hole pair. In single QDs, PL blinking (intermittent PL as a function of time) has been observed and

has been explained (Nirmal *et al.*, 1996; Efros and Rosen, 1997) by this type of Auger process ionising one carrier over the potential barrier at the surface into the surface region. This creates an electric dipole in the QD that quenches subsequent radiative emission after subsequent photon absorption; after some time, the ionised carrier can return to the QD core and the PL is turned on again. Since this Auger process can occur in QDs, the inverse Auger process, whereby one high-energy electron–hole pair (created from a photon with $h\nu > E_g$) can generate two electron–hole pairs, was predicted by Nozik to also occur in QDs (Nozik, 1997, 2001b and 2002).

The proposed Benisty mechanism (Benisty *et al.*, 1991; Benisty, 1995) for slowed hot-carrier cooling and phonon bottleneck in QDs requires that cooling only occur via LO phonon emission. However, there are several other mechanisms by which hot electrons can cool in QDs. Most prominent among these is an Auger mechanism (Efros *et al.*, 1995) where the excess energy of the electron is transferred again to the hole, which then cools rapidly because of its larger effective mass and smaller energy level spacing. Thus, an Auger mechanism for hot-electron cooling can break the phonon bottleneck (Efros *et al.*, 1995). Other possible mechanisms for breaking the phonon bottleneck include electron–hole scattering (Vurgaftman and Singh, 1994), deep-level trapping (Sercel, 1995), and acoustical-optical phonon interactions (Inoshita and Sakaki, 1992 and 1997).

As will be shown below, some degree of slowed cooling (a partial phonon bottleneck) can occur in certain QDs and QD configurations, leading to cooling times of several ps compared with several hundred fs in bulk and certain other QDs (a factor of about 10). But we shall also see that the process of creating multiple excitons from single photons in QDs is so unexpectedly fast that it easily beats the cooling time without requiring the very long cooling times (ns to μ s) that would be expected from a full phonon bottleneck.

Experimental determination of cooling dynamics of phonon bottlenecks in QDs

Over the past several years, many investigations have been published that explore hot electron cooling/relaxation dynamics in QDs and the issue of a phonon bottleneck in QDs. The results are controversial, and there are many reports that both support and contradict the prediction of slowed hot-electron cooling in QDs and the existence of a phonon bottleneck: Nozik (2001b) gives a detailed reference list. One element of confusion is that while some of these publications report relatively long hot electron relaxation times (tens of ps) compared with what is observed in bulk semiconductors, the results are reported as being not indicative of a phonon bottleneck because the relaxation times are not excessively long and PL is observed (Heitz *et al.*, 1998; Li

and Arakawa, 1998; Sosnowski *et al.*, 1998). Theory predicts very long relaxation lifetimes (hundreds of ns to μ s) of excited carriers for the extreme, limiting condition of a full phonon bottleneck; thus the carrier lifetime would be determined by non-radiative processes and PL would be absent. However, since the interest here is on the rate of relaxation/cooling compared with the rate of electron separation and transfer, and multiple-exciton generation (MEG), we consider that slowed relaxation/cooling of carriers has occurred in QDs if the relaxation/cooling times are $>3\text{--}5$ ps (about an order of magnitude greater than that for bulk semiconductors). This is because electron separation and transport and MEG can be very fast (sub-ps). For solar fuel production, previous work that measured the time of electron transfer from bulk III–V semiconductors to redox molecules (metallocenium cations) adsorbed on the surface found that electron transfer (ET) times can also be sub-ps to several ps (Miller *et al.*, 1995; Meier *et al.*, 1997 and 1999; Diol *et al.*, 1998); hence photoinduced hot-carrier separation, transport and transfer can be competitive with electron cooling and relaxation if the latter is longer than about 10 ps. MEG rates can also be in the sub-ps regime (Ellingson *et al.*, 2005; Schaller *et al.*, 2005a).

In a series of papers, Sugawara *et al.* (Mukai *et al.*, 1996; Sugawara *et al.*, 1997; Mukai and Sugawara, 1998) have reported slow hot electron-cooling in self-assembled InGaAs QDs produced by Stranski–Krastanov (SK) growth on lattice-mismatched GaAs substrates. Using time-resolved PL measurements, the excitation-power dependence of PL, and the current dependence of electroluminescence spectra, these researchers report cooling times ranging from 10 ps to 1 ns. The relaxation time increased with electron energy up to the fifth electronic state. Also, Mukai and Sugawara (1999) have published an extensive review of phonon bottleneck effects in QDs, which concludes that the phonon bottleneck effect is indeed present in QDs.

In addition to studies on self-assembled SK type of QDs, studies of carrier cooling and relaxation have also been performed on colloidal QDs by Klimov *et al.* (Klimov and McBranch, 1998; Klimov *et al.*, 2000), Guyot-Sionnest *et al.* (1999), Ellingson *et al.* (2003), and Blackburn *et al.* (2003). These results (Guyot-Sionnest *et al.*, 1999) support the Auger mechanism for electron relaxation, whereby the excess electron energy is rapidly transferred to the hole, which then relaxes rapidly through its dense spectrum of states. When the hole is rapidly removed and trapped at the QD surface, the Auger mechanism for hot-electron relaxation is inhibited and the relaxation time increases. Klimov (2000) provides a review of this work.

Blackburn *et al.* (2003) and Ellingson *et al.* (2003) have reported results for the electron-cooling dynamics in InP QDs, where the QD surface was modified to affect hole trapping and also where only electrons were injected into the QD from an external redox molecule (sodium biphenyl) so that the holes necessary for the Auger

cooling mechanism were not present in the QD (Blackburn *et al.*, 2003). For InP, HF etching was found to passivate electronic surface states, but not hole surface states (Langof *et al.*, 2002; Micić *et al.*, 2002); thus, holes can become localised at the surface in both etched and unetched TOPO-capped QDs, and the dynamics associated with these two samples will not deviate significantly. The relaxation was found to be bi-exponential and suggests the presence of two subsets of quantum dots within the sample (Blackburn *et al.*, 2003; Ellingson *et al.*, 2003). Since etching has been shown to passivate hole traps inefficiently, it was proposed that the two subsets of quantum dots should be probed in the experiment: one subset in which the hole and electron are efficiently confined to the interior of the nanocrystal (hole trap absent; exciton confined to the QD core), and one subset in which the hole is localised at the surface of the QD on a phosphorus dangling bond (hole trap present; charge-separated QD) (Blackburn *et al.*, 2003; Ellingson *et al.*, 2003).

With the electron and hole confined to the QD core, strong electron–hole interaction leads to efficient, fast relaxation via the Auger mechanism, and in QDs where the hole is localised at the surface, the increased spatial separation inhibits the Auger process and results in slower relaxation. The data imply that hole trapping at the intrinsic surface state occurs in less than 75 fs (Blackburn *et al.*, 2003).

To further investigate the mechanisms involved in the intraband relaxation, experiments were conducted in which only electrons were present in the QDs and holes were absent. Sodium biphenyl is a very strong reducing agent, which has been shown to inject electrons into the conduction band of CdSe QDs (Shim and Guyot-Sionnest, 2000; Shim *et al.*, 2001), effectively bleaching the 1S transition and allowing an IR-induced transition to the 1P_e level. Sodium biphenyl was therefore used to inject electrons into the 1S electron level in InP QDs (Blackburn *et al.*, 2003). This 1S_e electron may be excited to the 1P_e level with an IR pump and its relaxation dynamics monitored back to the ground 1S state. Time-resolved, IR-induced transitions in *n*-type (electron-injected) InP QDs show that the relaxation of the excited electrons from the 1P to the 1S level can be fitted to a single exponential, with an average time constant of 3.0 ps, corresponding to a relaxation rate of 0.092 eV ps⁻¹; in neutral 50 Å TOP/TOPO-capped InP QDs, the relaxation shows a large 400 fs component indicative of fast electron cooling. Similar conclusions were reported for electrons injected into ZnO and CdSe colloidal quantum dots (Guyot-Sionnest *et al.*, 2005). These experiments confirm that in the absence of a core-confined hole, electronic relaxation is slowed by about an order of magnitude. However, it should be noted that the relaxation rate in the absence of a hole is close to the relaxation rate with the hole localised at the surface. This is surprising and raises the question of why electron cooling in the absence of a hole is not longer. Possible explanations have

been proposed (Efros and Nozik, 2003) including that (1) positive counter ions of the oxidised sodium biphenyl are adsorbed on the QD surface and behave like a trapped hole in producing a significant Coulomb interaction with the electron to permit Auger cooling; and (2) an enhanced Huang-Rhys parameter occurs in charged QDs and enhances multiphonon relaxation.

Recent results obtained by Guyot-Sionnest *et al.* (2005) show that the nature of the surface ligands has a major effect on the relaxation dynamics. Depending on the surface ligand stabilising the QDs, the relaxation or cooling dynamics of hot excitons could be varied from 3.8 ps for tetradecylphosphonic acid, to 8 ps for oleic acid, 10 ps for octadecylamine, and 27 ps for dodecanethiol ligands. The later cooling rate is nearly two orders of magnitude slower than that for naked QDs or QDs capped with TOP-TOPO.

In contradiction to the results showing slowed cooling in QDs, many other investigations are reported in the literature in which a phonon bottleneck was apparently not observed. These results have been reported for both self-organised SK QDs and II–VI colloidal QDs: Nozik (2001b) gives a detailed reference list. However, in several cases (Heitz *et al.*, 1997; Heitz *et al.*, 1998; Sosnowski *et al.*, 1998), hot-electron relaxation was found to be slowed, but not sufficiently for the authors to conclude that this was evidence of a phonon bottleneck.

3.5 High conversion efficiency via multiple exciton generation in quantum dots

For a single-bandgap system, there are two fundamental ways in which hot carriers or excitons can be converted to useful work to enhance the efficiency of solar photon conversion. One way produces an enhanced photovoltage, and the other an enhanced photocurrent. As discussed above in Sections 3.1 and 3.4, the former requires that the hot carriers be extracted from the photoconverter before they cool (Boudreaux *et al.*, 1980; Ross and Nozik, 1982; Nozik, 2001b), while the latter requires the hot carriers to produce two or more electron–hole pairs (Kolodinski *et al.*, 1993; Landsberg *et al.*, 1993). This latter process is well known in bulk semiconductors and is termed *impact ionisation* (II); it is the inverse of the Auger process whereby two electron–hole pairs recombine to produce a single highly energetic electron–hole pair.

In order to achieve higher photovoltages, the rates of photogenerated carrier separation, transport and interfacial transfer across the semiconductor interface must all be fast compared with the rate of carrier cooling (Boudreaux *et al.*, 1980; Nozik, 1980; Williams and Nozik, 1984). The achievement of higher photocurrent requires that the rate of II (r_{II}) or electron–hole pair multiplication is greater than the rates of

carrier cooling (r_{cooling}), electron transfer ($r_{\text{ET}}^{\text{hot}}$) of hot electrons, and the forward Auger processes (r_{Auger}) (see Fig. 3.13). Also, the rate of electron transfer of cooled electrons (r_{ET}) must be faster than the radiative recombination rate (r_{rad}) and r_{Auger} . Thus the required inequalities are

$$r_{\text{MEG}} > r_{\text{ET}}^{\text{hot}}, r_{\text{cooling}}; r_{\text{Auger}} < r_{\text{MEG}}; r_{\text{ET}} > r_{\text{rad}} > r_{\text{Auger}}$$

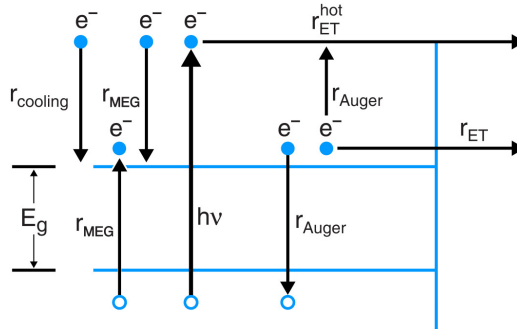


Figure 3.13 Various competing channels for hot-electron cooling. Source: Nozik (2005).

3.5.1 Cooling dynamics in quantum dots

As discussed above in Section 3.4, although the hot-carrier cooling rates are very fast in bulk semiconductors, the rates can be slowed down in quantised semiconductor structures because of the formation of discrete quantised energy levels. In quantum dots, photogenerated electrons and holes become bound to each other because of strong quantum confinement, and the correlated electron–hole pairs become excitons. The slowed cooling of energetic excitons can enhance the photon conversion efficiency by allowing electrical or chemical free energy to be extracted from the energetic excitons before they relax to their lowest electronic state and produce heat.

3.5.2 Electron–hole pair (exciton) multiplication in quantum dots

The formation of multiple electron–hole pairs per absorbed photon in photoexcited bulk semiconductors is a process typically explained by impact ionisation. In this process, an electron or hole with kinetic energy greater than the semiconductor bandgap produces one or more additional electron–hole pairs. The kinetic energy can

be created either by applying an electric field or by absorbing a photon with energy at least twice that of the semiconductor bandgap energy. The former is well studied and understood (Bude and Hess, 1992; Jung *et al.*, 1996; Harrison *et al.*, 1999). The latter process is less well studied, but has been observed in photoexcited *p-n* junctions of Si, Ge, and InSb (Tauc, 1959; Vavilov, 1959; Hodgkinson, 1963; Christensen, 1976).

However, impact ionisation has not contributed meaningfully to improved quantum yields in working solar cells, primarily because the II efficiency does not reach significant values until photon energies reach the ultraviolet region of the spectrum. In bulk semiconductors, the threshold photon energy for II exceeds that required for energy conservation alone because, in addition to conserving energy, crystal momentum must be conserved. Additionally, the rate of II must compete with the rate of energy relaxation by phonon emission through electron–phonon scattering. It has been shown that the rate of II becomes competitive with phonon scattering rates only when the kinetic energy of the electron is many times the bandgap energy (E_g) (Bude and Hess, 1992; Jung *et al.*, 1996; Harrison *et al.*, 1999). The observed transition between inefficient and efficient II occurs slowly; for example, in Si the II efficiency was found to be only 5% (*i.e.* total quantum yield = 105%) at $h\nu \approx 4$ eV ($3.6E_g$), and 25% at $h\nu \approx 4.8$ eV ($4.4E_g$) (Christensen, 1976; Wolf *et al.*, 1998). This large blue shift of the threshold photon energy for II in semiconductors prevents materials such as bulk Si and GaAs from yielding improved solar conversion efficiencies (Kolodinski *et al.*, 1993; Wolf *et al.*, 1998).

However, in quantum dots the rate of electron relaxation through electron–phonon interactions can be significantly reduced because of the discrete character of the electron–hole spectra, and the rate of Auger processes, including the inverse Auger process of exciton multiplication, is greatly enhanced owing to carrier confinement and the concomitantly increased electron–hole Coulomb interaction (see Fig. 3.14). Furthermore, crystal momentum need not be conserved because momentum is not a good quantum number for three-dimensionally confined carriers (from the Heisenberg Uncertainty Principle the well-defined location of the electrons and holes in the nanocrystal makes the momentum uncertain). Indeed, very efficient multiple electron–hole pair (multiexciton) creation by one photon has now been reported in six semiconductor QD materials: PbSe, PbS, PbTe, CdSe, InAs and Si. The first report was by Schaller and Klimov (2004) for PbSe NCs; they reported an excitation energy threshold for the efficient formation of two excitons per photon at $3E_g$, where E_g is the absorption energy gap of the nanocrystal (HOMO–LUMO transition energy). Schaller and Klimov reported a QY value of 218% (118% II efficiency) at $3.8E_g$; QYs above 200% indicated the formation of more than two excitons per absorbed photon. The NREL research group (Ellingson *et al.*, 2005) recently reported a QY value of 300%

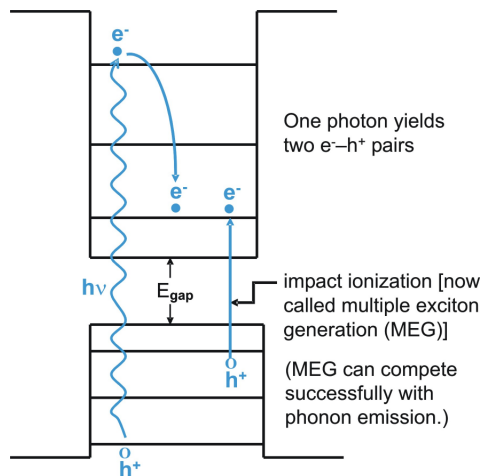


Figure 3.14 Multiple electron-hole pair (exciton) generation (MEG) in quantum dots.
Source: Nozik (2002).

for 3.9-nm diameter PbSe QDs at a photon energy of $4E_g$, indicating the formation of three excitons per photon for every photoexcited QD in the sample. The data also indicated that the sharp rise of MEG occurred more steeply and at a lower threshold photon energy with smaller-sized QDs. Evidence was also provided that the threshold energy for MEG by optical excitation is $2E_g$ (Ellingson *et al.*, 2005), and that efficient MEG also occurs in PbS (Ellingson *et al.*, 2005) and in PbTe nanocrystals (Murphy *et al.*, 2006). A new mechanism for MEG was introduced that invokes a coherent superposition of multiple excitonic states, meaning that multiple excitons are essentially created instantly on absorption of high-energy photons (Ellingson *et al.*, 2005; Shabaev *et al.*, 2006). This new model also explains the lower threshold photon energy for MEG at $2E_g$ for the IV–VI semiconductors (PbS, PbSe, PbTe) that have approximately equal effective masses for electrons and holes. This property led some authors (Schaller, 2004) to believe that the excess energy of the absorbed photon is split equally between the electron and hole, thus requiring a threshold of $3E_g$. However, several other models for MEG have also been proposed (Schaller *et al.*, 2005a; Franceschetti *et al.*, 2006).

Multiexcitons are detected by several spectroscopic measurements. The first one was to monitor the signature of multiexciton decay dynamics using transient absorption (TA) spectroscopy (Schaller and Klimov, 2004; Ellingson *et al.*, 2005; Schaller *et al.*, 2005b and 2006; Murphy *et al.*, 2006). The magnitude of the photo-induced absorption change at the band edge is proportional to the number of electron–

hole pairs created in the sample. In Ellingson *et al.* (2005) and Murphy *et al.* (2006), the transients are detected by probing either with a band edge (energy gap or HOMO–LUMO transition energy $\equiv E_g$) probe pulse, or with a mid-IR probe pulse that monitors intraband transitions in the newly created excitons. Our multiple exciton Auger recombination analysis relies only on data for delays >5 ps, by which time carrier multiplication and cooling are complete.

In Ellingson *et al.* (2005) and Murphy *et al.* (2006), the dependence of the MEG QY on the ratio of the pump photon energy to the bandgap (E_{hv}/E_g) varied from 1.9 to 5.0 for PbSe QD samples with $E_g = 0.72$ eV (diameter = 5.7 nm), $E_g = 0.82$ eV (diameter = 4.7 nm), and $E_g = 0.91$ eV (diameter = 3.9 nm), as shown in Fig. 3.15. For all three samples, the sharp rise in QY begins at about three times the energy gap. For the two PbSe samples with $E_g = 0.82$ eV (4.7 nm diameter) and 0.72 eV (5.7 nm diameter), it is estimated that a QY of 300% is reached at an E_{hv}/E_g value of 5.5. It was noted that the $2P_h$ – $2P_e$ transition in the QDs is resonant with the $3E_g$ excitation, corresponding to the sharp onset of increased MEG efficiency. If this symmetric transition ($2P_h$ – $2P_e$) dominates the absorption at $\sim 3E_g$, the resulting excited state provides both the electron and the hole with excess energy of $1E_g$ in resonance with the lowest exciton absorption (at $1E_g$). These data also showed that the QY begins to surpass 100% at E_{hv}/E_g values greater than 2.0 (see Fig. 3.15). We carefully measured sixteen QY values between $2.1E_g$ and $2.9E_g$ (mean value = 109.8%) and eleven QY values between $1.2E_g$ and $2.0E_g$ (mean value = 101.3%). Application of statistical t-

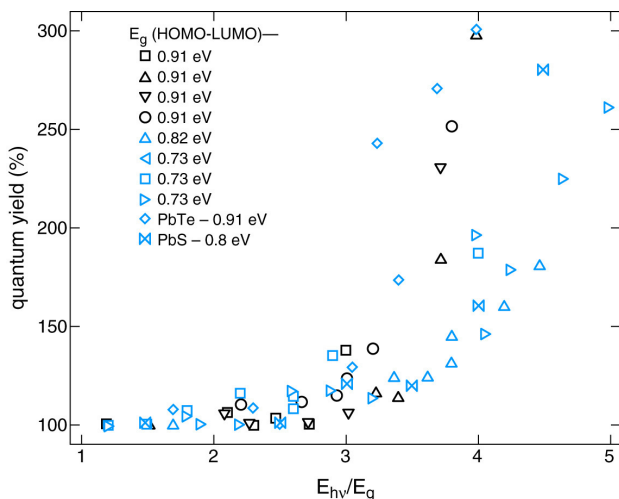


Figure 3.15 Quantum yield of MEG vs photon energy (E_{hv}/E_g) for PbSe, PbS, and PbTe QDs. The values for QD bandgaps (HOMO–LUMO) are listed next to the symbols.

tests showed that the QY values for photon energies between $1E_g$ and $2E_g$ were not statistically different from 100% (P value = 0.105), while the difference in QYs between $1.2E_g$ – $2.0E_g$ and $2.1E_g$ – $2.9E_g$ were very statistically significant with a P value of 0.001 (Ellingson *et al.*, 2005). Also, simple visual inspection of Fig. 3.15 shows a significant difference between the QY values between $1E_g$ – $2E_g$ and $2E_g$ – $3E_g$.

Additional experiments observing MEG have been reported for CdSe (Schaller *et al.*, 2005b), PbTe (Murphy *et al.*, 2006) and InAs (Pijpers *et al.*, 2007). In addition to transient absorption studies, these optical experiments use time-resolved photoluminescence, terahertz spectroscopy, and quasi-CW spectroscopy.

3.5.3 Theory of multiple exciton generation

In a novel recent theory of MEG (Shabaev *et al.*, 2006), efficient MEG by a single photon in NCs is explained by the formation of a coherent superposition of single- and multi-exciton states (see Fig. 3.16). The model uses a time-dependent density matrix approach, which allows simultaneous consideration of an arbitrary strength of coupling between single- and multi-exciton states, different dephasing rates for these states, and short pulse excitation of the NCs. The steady-state solution of the density matrix equations yields the following conditions for efficient MEG: (1) the energy relaxation rate of a single exciton (γ_1) initiated by light must be slower than both the energy relaxation rate of the multiexciton (γ_2) and the rate of Coulomb coupling between the two states ($W_C/\hbar$), where W_C is the matrix element of the Coulomb interaction between the single- and multi-exciton states:

$$W_C = \langle \psi_{1\text{Ex}} | q^2 / \epsilon |\mathbf{r}| | \psi_{n\text{Ex}} \rangle \quad (3.25)$$

and $\psi_{1\text{Ex}}$ is the initial single-exciton state, $\psi_{n\text{Ex}}$ is the multiexciton state, ϵ is the permittivity of the QD, and $\mathbf{r}$ is the vectorial distance between the electronic particles in the QD.

In the case of strong coupling, $\gamma_2 < W_C/\hbar$, MEG by a short light pulse is accompanied by quantum beats with the frequency $W_C/\hbar$. These oscillations are damped in the opposite case of weak coupling, $\gamma_2 > W_C/\hbar$; however, the MEG process can still be very efficient. The density matrix approach is the only self-consistent method that takes into account the diverse processes responsible for MEG in NCs.

Under optical excitation of NCs, a single photon can only generate a *single* electron–hole pair which is not an eigenstate of the multielectron Hamiltonian that describes the superposition of multiexcitons. This initial single electron–hole pair

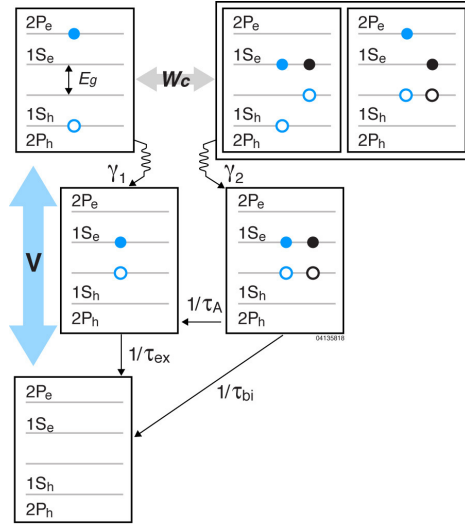


Figure 3.16 Theoretical model for MEG. For simplicity, only three degenerate states are shown following absorption of a $3E_g$ photon ($2P_h - 2P_e$): the initial single $2P_h 2P_e$ exciton, and the two excited biexciton states ($2P_h 1S_e 1S_h 1S_e$, $1S_h 1S_e 2P_e 1S_e$). For simplicity, the fourth state ($1S_h 1S_e 1S_h 1S_e 1S_e 1S_e$) is not represented and electronic states between the $1S$ and $2P$ states are also not shown. The three degenerate states are coupled by the Coulomb interaction (W_c) and form a coherent superposition of three states; their populations experience oscillations with time (quantum beats). The relaxation (cooling) rate of the single exciton state ($1/\gamma_1$) is slower than the relaxation rate of the biexciton states ($1/\gamma_2$) because of the asymmetric charge distribution in the excited biexcitons (the latter enhances electron–phonon coupling). This preferential dephasing of the coherence for the excited biexcitons results in the final formation of a biexciton from a single photon. V is the overall rate of decay of the excited single exciton to the ground state, while $1/\tau_{ex}$ and $1/\tau_{bi}$ are the rates of the decay of the relaxed (cooled) single exciton and biexcitons to the ground state. All of these latter three rates are slow compared with the rates of relaxation and Coulomb coupling. Source: Shabaev *et al.* (2006).

state (exciton) is coupled with the multiexciton states and creates a superposition of single and multiexcitons. Below, the theory is applied to PbSe NCs, in which the onset of very efficient MEG occurs at photon energies of $3E_g$, corresponding to a $2P_h \rightarrow 2P_e$ transition (Shabaev *et al.*, 2006) (but note that the threshold for the onset of MEG is $2E_g$).

For a strongly coupled superposition of single- and multi-exciton states, the question of MEG efficiency is reduced to the question of the state relaxation. The single- and multi-exciton components of the superposition have different decay rates, and the ratio of these rates determines what a single photon creates: a single exciton or multiexcitons.

To calculate the efficiency of MEG, it is necessary to compare the populations of the ground state (band-edge) biexcitons, N_{bi} , to the single exciton, N_{ex} , during time, t , which is much longer than the relaxation times of the excited states ($1/\gamma_1$ and $1/\gamma_2$, respectively) but much shorter than the lifetime of the band-edge excitons ($1/\Gamma_{ex}$ and $1/\Gamma_{bi}$); *i.e.* $1/\gamma_1 \leq 1/\gamma_2 \ll 1/\Gamma_{bi} \ll 1/\Gamma_{ex}$. This approach ultimately yields the ratio of the band-edge biexciton and single-exciton populations (Shabaev *et al.*, 2006)

$$N_{bi} / N_{ex} = (\gamma_2 / \gamma_1) P_{1-2} \quad (3.26)$$

where P_{1-2} is the probability of the population of the excited biexciton state via its Coulomb coupling to the excited single-exciton state created by a photon; the value of P_{1-2} is always < 1 .

Equation 3.26 shows that efficient MEG, *i.e.* the predominant generation of multiexcitons, is possible only if the relaxation rate of the biexciton is much faster than that of the exciton ($\gamma_2 \gg \gamma_1$), because $P_{1-2} < 1$. For strong coupling, the transition probability approaches unity and the population ratio approaches its maximum value of (γ_2/γ_1) . This result has a transparent physical meaning: for a strongly coupled superposition state, the populations of N_{bi} and N_{ex} are controlled by the state decay into the two independent thermalisation channels.

MEG, however, can be efficient even for a weak coupling regime, $W_C/\hbar \ll \gamma_2$. In this case $N_{bi}/N_{ex} = 4W_C^2/(\hbar^2 \gamma_1 \gamma_2)$, and can be much larger than unity if $W_C/\hbar \gg \gamma_1$ (Shabaev *et al.*, 2006). The relative population N_{bi}/N_{ex} is then determined by the ratio of the biexciton creation rate, $(2W_C/\hbar)^2\gamma_2$, to the direct single-exciton relaxation rate, γ_1 .

As discussed above, MEG has been observed by measuring the bleaching of the optical absorption at the bandgap frequency. Although the initially excited exciton, whose energy is above the MEG threshold, does not directly populate the states at the bandgap, the bleaching increases rapidly after the excitation. The timescale of the bleaching evolution provides information about the strength of the coupling between the initially excited state and the multiexcitons which populate the low-energy states at the bandgap. Efficient MEG leads to bleaching that significantly exceeds the bleaching of the single band-edge exciton. In the excitation frequency range for the $2P_h \rightarrow 2P_e$ transition, the time dependence of the relative change (bleach) of the band-edge absorption after a short pulse excitation is shown in Fig. 3.17. This figure shows that strong coupling ($W_C/\hbar > \gamma_2$) significantly shortens the bleach rise time ($\sim \hbar/W_C$) and leads to quite pronounced oscillations (quantum beats) resulting from the creation of the coherent superposition of the single- and bi-exciton excited states. The coherent oscillations become overdamped even for a relatively strong coupling if $W_C/\hbar \sim \gamma_2$,

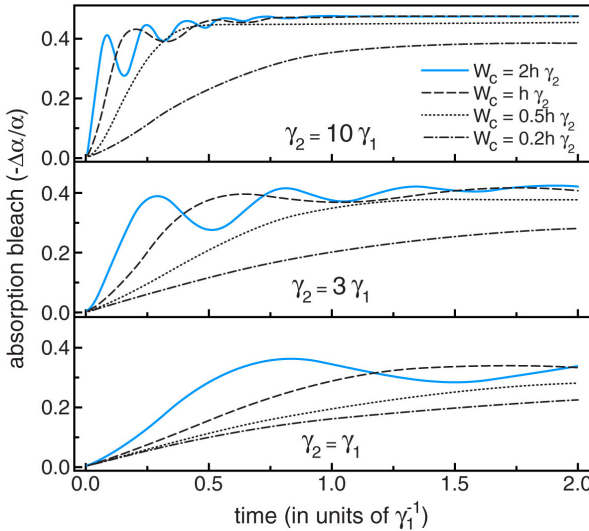


Figure 3.17 Time evolution of the $1S_e 1S_h$ exciton population as a function of the relaxation times and Coulomb coupling for the single and biexcitons. The rise time of the biexciton (formation time) and the presence of strong or damped quantum beating depends upon the relative values of the W_c , γ_1 , and γ_2 as shown above. Source: Shabaev *et al.* (2006).

and the coupling still substantially mixes the exciton states. In the weak coupling regime, $W_c/\hbar < \gamma_2$, the bleach rise time is slowed down by the biexciton decay rate and is proportional to $\hbar^2 \gamma_2 / W_c^2$.

Detuning of the resonance between single- and multi-exciton states, for example from a significant size dispersion of the NC population, also affects the bleach rise-time behaviour. Generally, the detuning increases the frequency of the beats and slows down the formation of a coherent superposition. Thus, a significant NC size dispersion will wash out pronounced quantum beats and slow down the average rise time of the bleach signal. This appears to be the case for the rise-time data in Ellingson *et al.* (2005), where only an apparent half-oscillation is observed.

Although the major mechanism for carrier thermalisation in NCs is still not agreed upon, it is found theoretically (Shabaev *et al.*, 2006) that the biexciton relaxation rate is much faster than the single-exciton relaxation rate, assuming that the relaxation rate for various electron-hole pair configurations is proportional to their coupling with phonons. These calculations show that polar interactions of intrinsic semiconductor phonons in CdSe and PbSe NCs with asymmetric electron-hole pair configurations are 10–40 times stronger than that of their coupling with symmetric electron-hole pair

configurations ($nL_e nL_h$). This is because in the latter case, charge distributions of the optically created electron and hole compensate each other almost exactly at each point of the NC, and the NC thus retains its local neutrality even after exciton creation. As a result, exciton interactions with the polar optical phonons that are sensing the total charge are very weak (Schmitt-Rink *et al.*, 1987). It is also quite obvious that the coupling of asymmetric electron-hole configurations with phonons of organic molecules at the NC surface (Guyot-Sionnest *et al.*, 2005) should be significantly stronger as well. In both cases, weak coupling of symmetric electron-hole pairs created by light with phonons suppresses their relaxation and would result in efficient MEG because the condition $\gamma_1 \ll \gamma_2$ is fulfilled.

Efficient MEG also requires strong coupling between exciton and biexciton states relative to γ_1 : $W_C/\hbar \gg \gamma_1$. Fulfilling this condition satisfies the obvious requirement that the exciton thermalisation time should be longer than the coupling time between the optically created exciton and the asymmetric biexciton state (Nozik, 2002).

Experimental results indicate that $1/\gamma_1 \sim 2\text{--}6$ ps, depending on the NC size (Guyot-Sionnest *et al.*, 1999; Ellingson *et al.*, 2005; Harbold *et al.*, 2005; Schaller *et al.*, 2005c), and Shabaev *et al.* (2006) reported that the condition $W_C/\hbar \gg \gamma_1$ is fulfilled even for the lowest estimation of W_C . In NCs, the dielectric constant, $\epsilon(a)$, is smaller than in bulk, and consequently the coupling W_C is stronger.

Theoretically, the MEG QY will not show a size dependence if it is assumed that the ratio γ_1/γ_2 does not depend on size. At the same time, an increase of γ_2/γ_1 always leads to an increase of QY. The predicted size independence of the average number of electron-hole pairs generated via excitation of the same optical transition is consistent with experimental results, which show that the QY depends only weakly on size and is a function primarily of only one parameter: E_h/E_g (Schaller and Klimov, 2004; Ellingson *et al.*, 2005; Murphy *et al.*, 2006; Schaller *et al.*, 2006).

3.5.4 Thermodynamic calculations of conversion efficiency in MEG QD solar cells

Detailed balance model

Hanna and Nozik (2006) have used the detailed balance model to calculate the power conversion efficiency of single-gap and two-gap tandem solar conversion devices which employ QD absorbers capable of MEG after photon absorption. The detailed balance model has been used previously (Shockley and Queisser, 1961; Werner *et al.*, 1994; Spirkel and Ries, 1995; Brendel *et al.*, 1996; Würfel, 1997; de Vos and Desoete, 1998; Landsberg and Badescu, 2002) to calculate the limiting efficiency of ideal solar

cells with a single bandgap having greater than unity QY resulting from the process of impact ionisation. We will apply this model to calculate the efficiency of single-gap and two-gap tandem PV and photoelectrochemical (PEC) devices having various combinations of MEG absorbers. Here, the designation PEC refers to a solar-driven photoelectrolysis cell for the production of H_2 from H_2O .

The current-versus-voltage dependence for a single-threshold device is written as

$$I(V, E_g) = I_G(E_g) - I_R(V, E_g) \quad (3.27)$$

where I_G is the photogenerated current, I_R is the recombination current associated with radiative emission, E_g is the absorption threshold or bandgap of the absorber, and V is the photovoltage generated by the cell. Expressions for the photogenerated current I_G and recombination current I_R for a single-gap cell are written as

$$I_G(E_g) = q \int_{E_g}^{E_{\max}} QY(E) \Gamma(E) dE \quad (3.28)$$

$$I_R(V, E_g) = qg \int_{E_g}^{\infty} \frac{QY(E)E^2}{\exp\{[E - qQY(E)V]/kT\} - 1} dE \quad (3.29)$$

where E is the photon energy, q is the electronic charge, k is Boltzmann's constant, T is the temperature of the device (here $T = 300$ K), and $g = 2\pi/c^2h^3$, where c is the speed of light in vacuum and h is Planck's constant. The quantum yield, $QY(E)$, allows for the generation and recombination of multiple charge pairs per photon over the appropriate energy range. The unconcentrated ASTM G-173-3 solar spectrum¹ is used as the illumination source; $\Gamma(E)$ is the photon flux associated with the AM1.5G spectrum. $E_{\max}$ is the maximum photon energy in the solar spectrum; for AM1.5G, $E_{\max} = 4.428$ eV. For practical purposes, $E_{\max} \sim 4$ eV, because the integrated solar current above 4 eV in the standard AM1.5G spectrum is only $\sim 5 \mu A \text{ cm}^{-2}$. In eq. 3.28, we neglect carrier generation from ambient blackbody radiation, which is a good approximation for $E_g \geq 0.2$ eV. Implicit in eqs. 3.27–3.29 are the assumptions of the detailed balance model: all photons with energy above the absorption threshold are absorbed, the quasi-Fermi level separation is constant and equal to qV across the device (this is equivalent to the assumption of infinite carrier mobility), and the only active recombination mechanism is radiative recombination.

MEG is incorporated into the model through the energy-dependent quantum yield, $QY(E)$, for photon to carrier generation, which may exceed one over certain photon

¹ The ASTM G-173-3 Reference Solar Spectra can be found at <http://redc.nrel.gov/solar/spectra/am1.5/>.

energy ranges. The functional form for $QY(E)$ to model the quantum yield for ideal MEG QD absorbers is given by a sum of step functions

$$QY(E) = \sum_{m=1}^M \theta(E, mE_g) \quad (3.30)$$

where $\theta(E, mE_g)$ is the Heaviside unit step function. Taking $M = 1$ gives the usual assumption of one electron–hole pair generated on absorption of one photon. Setting $M = M_{\max} = E_{\max}/E_g$ gives the maximum possible multiplication allowed by energetic constraints and the highest possible efficiency for a MEG device. In the following, we denote MEG absorbers with $M = 1$, $M = 2$, and $M = M_{\max}$ as M1, M2, and $M_{\max}$, respectively.

The photovoltaic power conversion efficiency $\eta_{PV}(V)$ at a given operating point (I, V) is given by

$$\eta_{PV}(V) = I(V)V / P_{\text{in}} \quad (3.31)$$

where $P_{\text{in}} = 100 \text{ mW/cm}^2$ is the integrated optical power in the AM1.5G spectrum. The photoelectrochemical conversion efficiency for the production of stored chemical energy as H_2 from water splitting is written as

$$\eta_{\text{H}_2}(V) = I(V)U_{\text{H}_2} / P_{\text{in}} \quad (3.32)$$

where $U_{\text{H}_2} = 1.23 \text{ V}$ is the minimum thermodynamic potential required for water splitting at 300 K. In actual water-splitting devices, the operating or bias point of the cell V will be larger than U_{H_2} by the sum of the anode and cathode overpotentials and the resistive potential drop of the electrolyte. We will use V_{over} to denote the sum of these overpotentials (losses) and assume that it is independent of current. Then the operating voltage is

$$V = V_{\text{over}} + U_{\text{H}_2} \quad (3.33)$$

The maximum efficiency for a single-gap device with a given absorption threshold and QY can be found from eqs. 3.27–3.31 by maximising the efficiencies in eqs. 3.32 and 3.33 with respect to the operating voltage V . For two-gap tandem devices, the top and bottom cells are connected in series optically, but they can be connected electrically either in series or parallel. The subscript 1 denotes parameters for the top cell and 2 for the bottom cell. For a series-connected tandem device, the total current must be the same in each cell, while the photovoltage across the device is the sum of the voltages developed across each cell. For a parallel-connected tandem device, the photovoltage is equal to the voltage across the sub-cells, and the total current is the sum of the currents generated by each cell. For both PV and water-splitting tandem

devices, a restriction on the possible combinations of E_1 and E_2 arises from the requirement that a portion of the solar spectrum must be absorbed in the bottom cell for a tandem device to function. For all absorber combinations of top and bottom cells, the absorption threshold for the top cell must be larger than the absorption threshold of the bottom cell. Additionally, a water-splitting tandem device must have a combination of threshold energies E_1 , E_2 that generates an open-circuit voltage greater than $V_0 + U_{\text{H}_2}$ for the device to be able to split water.

Single-bandgap PV cells

The efficiency of ideal single-gap PV devices with carrier multiplication arising from an impact ionisation process has been reported by several authors (Werner *et al.*, 1994; Spirkel and Ries, 1995; Brendel *et al.*, 1996; Würfel, 1997; de Vos and Desoete, 1998; Landsberg and Badescu, 2002). In these publications, blackbody solar illumination was assumed for the solar spectrum. Under the AM1.5G spectrum (integrated incident solar power = 100 mW cm^{-2}), the maximum efficiency for single-gap cells operating at 300 K with the quantum yields of eqs. 3.31–3.33 is shown in Fig. 3.18. The curve labelled M_1 has no carrier multiplication and corresponds to the Shockley–Queisser limit with a maximum efficiency 33.7% occurring at $E_g = 1.34 \text{ eV}$.² The efficiency curve labelled M_{max} is calculated using the maximum possible integral number of multiplications consistent with the constraint imposed by the available excess energy $M_{\text{max}} = E_{\text{max}}/E_g$. The maximum efficiency for a single-gap

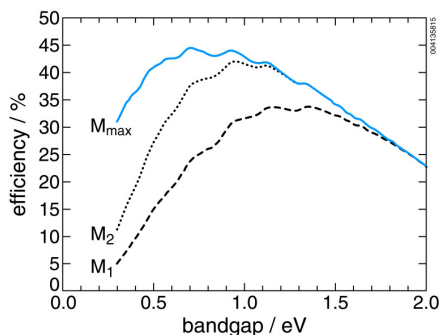


Figure 3.18 PV conversion efficiency as a function of QD bandgap for single-gap devices with the following absorber types: M_1 (no exciton multiplication), M_2 (two excitons per photon above $h\nu = 2E_g$), and M_{max} (maximum possible number of excitons per photon from solar spectrum).

² Values of the Shockley–Queisser limiting efficiency differing by a few absolute percent appear in the literature because of differences in the incident spectra or operating temperature used in the calculations.

MEG PV device is 44.4% for bandgap $E_g = 0.7$ eV, where $M_{\max} = 6$. This is similar to the value reported by de Vos and Desoete (1998) for a blackbody-illuminated PV device with maximum carrier multiplication. It is interesting to note that a high efficiency of ~42% is still obtained with a multiplication of only 2 (curve labelled M_2), which is 94% of the absolute maximum. This means that high multiplication values (>2) are not essential for substantially increasing the efficiencies of single-gap PV devices having carrier multiplication absorbers.

Tandem cells with two bandgaps for water splitting

Calculations by Hanna and Nozik (2006) show that the conversion efficiency of two-gap tandem cells for PV that exhibit MEG does not improve significantly compared with two-gap tandem cells with no MEG occurring in any of the tandem layers. The maximum value for all two-gap tandem combinations is ~45% at one Sun. For water-splitting cells with no MEG, the maximum efficiency (with zero overvoltage) increases from ~31% using a single-gap photoelectrode to ~41% using a two-gap tandem cell configuration. The optimum bandgaps for the latter case at zero overvoltage are 1.4 eV for the top cell and 0.5 eV for the bottom cell; for the former case, the optimum bandgap is 1.31 eV for zero overvoltage. For an overvoltage V_{over} of 0.6 V, the maximum efficiency for a single-gap cell is 13%, and for the tandem cell it is 33%. The optimum bandgaps for these two cases are 2.13 eV for the single-gap cell, and 1.6 eV and 0.9 eV for the tandem cell. However, the efficiencies of both single-gap and tandem photoelectrolysis cells increase only modestly with MEG.

Conclusions about conversion efficiencies with MEG solar cells

Solar conversion devices with MEG absorbers have in some cases higher limiting efficiencies than devices without MEG. The largest increase in efficiency over the case with no MEG occurs for single-gap PV devices, where the limiting efficiency increases by about one third, from 33.7% to 44.4% for maximum carrier multiplication. An increase in efficiency from 30.6% to 32.0% occurs when incorporating a M_2 MEG absorber into a single-gap photoelectrolysis cell. For the single-gap PV efficiency, increasing the multiplication above M_2 will not improve the efficiency of a single-gap photoelectrolysis device above that obtained with M_2 . The smaller improvement in efficiency of single-gap photoelectrolysis devices is due to the additional constraint imposed on the photovoltage by the minimum free energy required for water splitting. In PV devices, the voltage at the maximum power point is not restricted as for the photoelectrolysis devices, allowing higher efficiency to be

obtained at lower bandgaps where the increased current from MEG outweighs the reduction in voltage.

In tandem PV devices, the inclusion of MEG in either top or bottom cells improves the efficiency when the top cell has an M2 absorber, but the increase is relatively small—only about 2%. A MEG absorber improves the efficiency of a tandem photoelectrolysis device to a greater degree than a tandem PV device, although the efficiency of the photoelectrolysis device is slightly lower than the PV device with the same configuration. The introduction of overvoltage losses in photoelectrolysis devices with MEG shows that they lose their advantage over normal photoelectrolysis devices for overpotentials above 0.4 V. At low overpotentials, single-gap and tandem devices with MEG absorbers have higher efficiencies than devices without MEG. For single-gap devices, the efficiency of the M1 and M2 devices becomes equal above $V_{\text{over}} = 0.4$ V. As V_{over} increases, larger bandgaps for both the top and bottom cells in a tandem device are required to obtain sufficient photovoltage to overcome the losses and drive the water-splitting reaction. In general, careful analyses of the efficiencies are required before concluding that a solar converter with a MEG absorber will perform better than a device without MEG.

3.6 Quantum dot solar cell configurations

There are two fundamental approaches for enhancing the solar photon conversion efficiency: increased photovoltage (Boudreaux *et al.*, 1980; Ross and Nozik, 1982) and increased photocurrent (Kolodinski *et al.*, 1993; Landsberg *et al.*, 1993). These can be accessed, in principle, in at least three different QD solar cell configurations; these configurations are shown in Fig. 3.19 and described below.

3.6.1 Photoelectrodes composed of quantum dot arrays

In this configuration, the QDs are formed into an ordered three-dimensional array with inter-QD spacing sufficiently small such that strong electronic coupling occurs and minibands are formed to allow long-range electron transport (see Fig. 3.19a). The optimum shape of QDs for this configuration is in the form of cubes rather than spheres, in order to get all inter-QD surfaces as close as possible. This system is a 3-D analogue to a one-dimensional superlattice and the miniband structures described above in Section 3.2 (see Fig. 3.4).

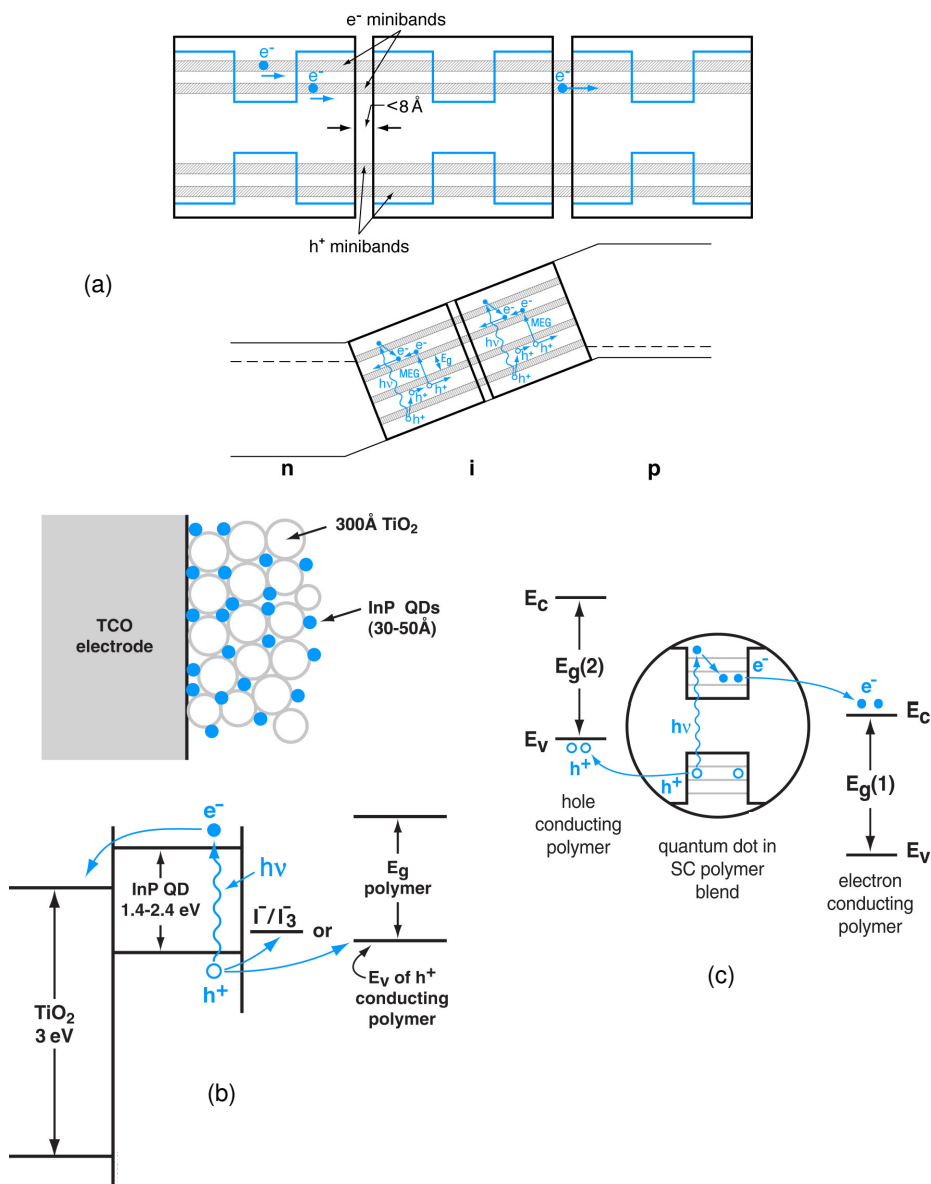


Figure 3.19 Configurations for QD solar cells. (a) A QD array used as the i region of a p - i - n junction cell configuration; (b) QDs used to sensitise a nanocrystalline film of TiO_2 to visible light. This configuration is analogous to the dye-sensitised solar cell with the dye replaced by QDs; (c) QDs dispersed in a blend of electron- and hole-conducting polymers. In these configurations the occurrence of MEG could produce higher photocurrents and higher conversion efficiency. Source: Nozik (2002).

The delocalised quantised 3-D miniband states could be expected to slow the carrier cooling and permit the transport and collection of hot carriers to produce a higher photopotential in a PV cell or in a photoelectrochemical cell where the 3-D QD array is the photoelectrode (Nozik, 1996). Also, MEG might be expected to occur in the QD arrays, enhancing the photocurrent (see Fig. 3.14). However, hot-electron transport/collection and MEG cannot occur simultaneously; they are mutually exclusive and only one of these processes can be present in a given system.

Significant progress has been made in forming cubic and spherical 3-D arrays of both colloidal (Mićić *et al.*, 1998 and 2001; Murray *et al.*, 2000) and epitaxial (Sugawara, 1999) II–VI and III–V QDs. The former have been formed via evaporation and crystallisation of colloidal QD solutions containing a uniform QD size distribution; crystallisation of QD solids from broader size distributions leads to close-packed QD solids, but with a high degree of disorder. Concerning the latter, arrays of epitaxial QDs have been formed by successive epitaxial deposition of epitaxial QD layers; after the first layer of epitaxial QDs is formed, successive layers tend to form with the QDs in each layer aligned on top of one other (Nakata *et al.*, 1999; Sugawara, 1999). Theoretical and experimental studies of the properties of QD arrays are currently under way. Major issues are the nature of the electronic states as a function of inter-dot distance, array order *versus* disorder, QD orientation and shape, surface states, surface structure/passivation, and surface chemistry. Transport properties of QD arrays are also of critical importance. Initial results show significant transport in close-packed QD arrays (Beard *et al.*, 2003; Murphy *et al.*, 2006).

3.6.2 Quantum dot-sensitised nanocrystalline TiO_2 solar cells

This configuration is a variation of the promising new type of photovoltaic cell discussed above and in Chapter 8 which is based on dye sensitisation of nanocrystalline TiO_2 layers (Moser *et al.*, 1998, Grätzel, 2000; Hagfeldt and Grätzel, 2000). In this cell, dye molecules are chemisorbed onto the surface of 10–30 nm-size TiO_2 particles that have been sintered into a highly porous nanocrystalline 10–20 μm TiO_2 film. On photoexcitation of the dye molecules, electrons are very efficiently injected from the excited state of the dye into the conduction band of the TiO_2 , effecting charge separation and producing a photovoltaic effect. The cell circuit is completed using a non-aqueous redox electrolyte that contains a I^-/I_3^- redox relay and a Pt counter electrode to allow reduction of the adsorbed photooxidised dye back to its initial non-oxidised state (via I_3^- produced at the Pt cathode by reduction of I^-).

For the QD-sensitised cell, QDs are substituted for the dye molecules, as shown in Fig. 3.19b; they can be adsorbed from a colloidal QD solution (Zaban *et al.*, 1998) or produced *in situ* (Weller, 1991; Liu and Kamat, 1993; Vogel *et al.*, 1994; Hoyer and Könenkamp, 1995). Successful PV effects in such cells have been reported for several semiconductor QDs including InP, CdSe, CdS, PbS and InAs (Weller, 1991; Liu and Kamat, 1993; Vogel *et al.*, 1994; Hoyer and Könenkamp, 1995; Zaban *et al.*, 1998; Nozik, 2001a; Robel *et al.*, 2006; Yu *et al.*, 2006; Tachibana *et al.*, 2007). Possible advantages of QDs over dye molecules are the tunability of optical properties with size, better heterojunction formation with solid hole conductors, and the unique potential capability of the QD-sensitised solar cell to produce quantum yields greater than one by MEG (inverse Auger effect) (Nozik, 2002).

3.6.3 Quantum dots dispersed in organic semiconductor polymer matrices

Photovoltaic effects have been reported in structures consisting of QDs forming junctions with organic semiconductor polymers. In one configuration, a disordered array of CdSe QDs is formed in a hole-conducting polymer—MEH-PPV (poly(2-methoxy, 5-(2'-ethyl)-hexyloxy-*p*-phenylenevinylene) (Greenham *et al.*, 1996). On photoexcitation of the QDs, the photogenerated holes are injected into the MEH-PPV polymer phase and are collected via an electrical contact to the polymer phase. The electrons remain in the CdSe QDs and are collected through diffusion and percolation in the nanocrystalline phase to an electrical contact to the QD network. Initial results showed relatively low conversion efficiencies (Greenham *et al.*, 1996 and 1997; Choi *et al.*, 2006; Cui *et al.*, 2006), but Huynh *et al.* (1999) reported improvements with rod-like CdSe QD shapes embedded in poly(3-hexylthiophene) (the rod-like shape enhances electron transport through the nanocrystalline QD phase). In another configuration (Arango *et al.*, 1999), a polycrystalline TiO₂ layer is used as the electron-conducting phase, and MEH-PPV is used to conduct the holes; the electron and holes are injected into their respective transport media on photoexcitation of the QDs.

A variation of these configurations is to disperse the QDs into a blend of electron- and hole-conducting polymers (see Fig. 3.19c). This scheme is the inverse of light-emitting diode structures based on QDs (Colvin *et al.*, 1994; Dabbousi *et al.*, 1995; Schlamp *et al.*, 1997; Mattoussi *et al.*, 1998; Mattoussi *et al.*, 1999). In the PV cell, each carrier-transporting polymer would have a selective electrical contact to remove the respective charge carriers. A critical factor for success is to prevent electron–hole recombination at the interfaces of the two polymer blends; prevention of electron–hole recombination is also critical for the other QD configurations mentioned above.

All of the possible QD-organic polymer photovoltaic cell configurations would benefit greatly if the QDs could produce multiple electron-hole pairs via MEG. This is also true for all the QD solar cell systems described in Section 3.6. The various cell configurations simply represent different modes of separating, collecting and transporting the photogenerated carriers produced in the QDs.

3.7 Summary and conclusions

Size quantisation in semiconductors greatly affects the relaxation dynamics of photo-induced carriers. These effects include slowed hot electron relaxation (phonon bottleneck) and enhanced Auger processes, including very efficient multiple exciton generation (MEG). The theoretical and measured energy threshold for carrier multiplication (impact ionisation) in bulk semiconductors (*e.g.* Si and Ge) is 4–5 times the bandgap. Much lower thresholds are predicted and confirmed for QDs because of the relaxation of the requirement to conserve crystal momentum. Very efficient MEG has been experimentally observed in PbSe, PbS, PbTe, CdTe, and InAs QDs; threshold photon energies as low as $2E_g$ have been reported. Up to 3 electrons per photon (300% QY) have been observed at sufficiently high photon energies ($>4E_g$). A new model based on a coherent superposition of multiexcitonic states has been introduced to explain these results, but other models for MEG have also been proposed. Two excitons/photon yield over 90% of the efficiency benefit of MEG. Various configurations of QD solar cells are possible that could yield high conversion efficiencies; these include: nanocrystalline TiO_2 sensitised with QDs, QD arrays that exhibit 3-D miniband formation used as the *i*-region in *p-i-n* structures, and QDs embedded in a blend of electron- and hole-conducting phases (for example, conducting polymers). The dynamics of hot exciton cooling, forward and inverse Auger recombination (MEG), and electron transfer can be modified and controlled in QD solar cells to potentially allow very efficient solar photon conversion via efficient MEG. To date the efficiency of QD solar cells is rather low ($<2\%$), but with further research and development it is expected the efficiency of such cells will improve markedly and lead to low-cost solar power

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CHAPTER 4

FUNDAMENTALS AND APPLICATIONS IN ELECTRON-TRANSFER REACTIONS

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When I happened in 1955 to see Libby's article, written in 1952, the electron transfer problem seemed merely an interesting puzzle. I didn't think in terms of it being the subsequent source of numerous applications. And perhaps that's the way it typically is in new directions in research.

From R. A. Marcus (1999), *Adv. Chem. Phys.* **106**, 1–6.

4.1 Introduction

Electron transfer (ET) is probably the most common and important mode of chemical reaction, as well as being fundamental to all electrochemical reactions. Processes as diverse as respiration, exciton dissociation, the rusting of iron, the luminescence of a glow worm and the decay of a corpse are all initiated by the transfer of an electron from an electron donor D to an electron acceptor A¹



where D and A may both be molecular entities or one may be an electronic conductor such as a nanoparticle or electrode. D and A may be nearest neighbours, either because they are directly linked to one another by a covalent bond in a D–A dyad or because they have come together in a collision complex. However, electron transfer—unlike other chemical reactions—does not require D and A to be in close contact, but remains possible where they are separated by several molecular diameters. In designed architectures, the separator is usually a bridge (B) of one or more intervening units in a DBA *super-*

¹ D and A are represented as neutral species for simplicity, although often one or both is charged (and electrostatic effects can influence ET rates). When both D and A really are neutral, the forward electron transfer is sometimes referred to as *charge separation* (CS) and the back reaction as *charge recombination* (CR). When D or A bears a charge, forward ET is sometimes referred to as a *charge-shift reaction*.

molecule, or a matrix structure such as a zeolite or clathrate in which D and A are held a fixed distance apart. Depending on the nature of the intervening bridge or medium, electron transfer may occur over D-to-A edge-to-edge distances r_{DA} of 20 Å or even more.

Where D and A are in close contact or are strongly coupled, electron transfer is usually *adiabatic*, meaning that every excursion along the reactant potential energy surface that reaches the transition barrier traverses across it to the product surface, *i.e.* the transmission coefficient κ_{el} for the reaction is 1. Where D and A are weakly coupled or separated by a relatively short edge-to-edge distance, electron transfer becomes *nonadiabatic* (sometimes equivalently termed *diabatic*), meaning that most excursions along the reaction coordinate do not result in reaction so $\kappa_{\text{el}} \ll 1$. (Figure 4.11 shows the difference between adiabatic and nonadiabatic electron transfer diagrammatically.)

In a covalently linked D–B–A supermolecule, *superexchange* is an important mechanism of nonadiabatic electron transfer. Here the electron tunnels coherently through a virtual state or virtual states formed by overlapping bridge orbitals of considerably greater energy than that of the tunnelling charge. The rate of electron transfer by this mechanism falls off exponentially with r_{DA} and becomes too slow to be significant where there are more than four or five intervening molecular units between D and A. Over longer distances than this, electron transfer if it occurs at all, occurs by incoherent *charge hopping*, in which the moving electron briefly populates one or more intervening states of the intervening bridge or medium and the coherence of the travelling electron wave is lost.

When one of the reaction partners in eq. 4.1 is in an electronically excited state, energy-storing photoinduced electron transfer (PET) reactions such as



between reactants A and D that do not react in the dark because reaction 4.1 is endergonic (having a positive Gibbs energy of reaction, ΔG°) become possible. Such reactions, often in covalently linked D–A or D–B–A structures, underlie many photoconversion processes. Compared with molecular photochemical energy storage reactions such as photoisomerisations, PET photoconversion reactions usually have more favourable threshold wavelengths, can be incorporated into a wider range of nanostructures and macrostructures, and are less prone to side reactions.

There is, however, a snag. ET reactions can go backwards as well as forwards without the symmetry restrictions that act on some molecular photochemical rearrangements to confer long-term metastability on the energy-rich products of the forward reaction. The back ET reaction



between the primary products of an energy-storing (endergonic) PET process is therefore not only thermodynamically spontaneous (having a negative Gibbs energy of reaction, ΔG°), but is likely also to be kinetically fast (having a low Gibbs energy of activation, $\Delta G^\ddagger$). Back electron transfer dissipates the energy of the primary photoproducts as heat and can rob PET systems of any useful net energy-storage efficiency.

Fortunately, there is a powerful way of slowing highly exergonic ET reactions, by operating in the so-called ‘inverted region’ in which $\Delta G^\ddagger$ increases and ET rates decrease even as the thermodynamic driving force $-\Delta G^\circ$ of the reaction increases. This can slow the rates of highly exergonic reactions by factors of up to $\sim 10^4$. Evolution, never slow to exploit a smart idea, seems to have placed the unwanted primary back electron transfers of natural photosynthesis in the inverted region, and many artificial photosynthetic systems employ or at least attempt the same stratagem.

There are other ways to discourage primary back ET, for example by locating the reacting components in structures that take advantage of electrostatic or hydrophobic interactions to stabilise or separate the primary products. A further stratagem, also employed in nature, is to add one or more secondary electron donors and/or acceptors in a redox chain, down which the ‘hole’ and ‘electron’ briefly lodged on the primary photo-products are rapidly led away from one another by successive electron transfers, as shown in Fig. 4.1. It is important that as little energy as possible be lost in each step, so that the fraction $\Delta G^\circ/E_{00}^S$ of the excited-state energy stored as chemical free energy in the final products (D_2^+ and A_2^- in Fig.4.1), is still appreciable.

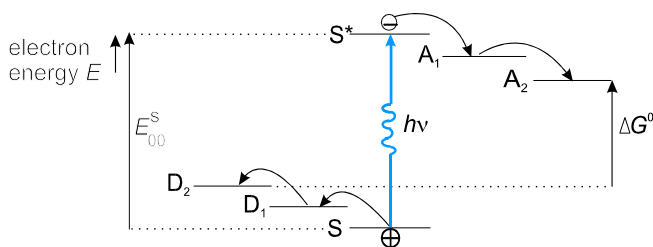


Figure 4.1 Schematic multistep energy-storing PET/ET process. Excitation of the sensitiser S produces a hole–electron pair on S^* . The electron then passes down the acceptor chain $A_1, A_2\dots$ and the hole down the donor chain $D_1, D_2\dots$

Transfer of an electron in one direction is equivalent to transfer of a hole in the other, which is convenient because it allows ET and HT (hole transfer) to be treated within the same theoretical framework. PET from a thermalised excited state can also be treated

within the same framework because it is effectively thermal ET (or HT) from an energetic and short-lived, but otherwise normal, molecule. Only where the reaction is very fast does the equivalence between ET, HT and PET fail. The hot electron processes discussed by Nozik in the next chapter are an important and fruitful case where the equivalence between ET and PET fails.

The rates of coherent ET, HT and PET are highly sensitive to, and primarily determined by, the distance r_{DA} between the electron donor D and the electron acceptor A, usually falling off exponentially by a factor of 2–5 for every 1 Å increase in r_{DA} , up to the limit of four or five intervening molecular units in most assemblies, where coherent ET yields to incoherent hopping or ceases altogether. Other major determinants of ET rates are: the strength of coupling between the donor and acceptor, and whether that coupling goes ‘through space’ by orbital overlap or ‘through bond’ via an intervening bridge of a few molecular units; and the extent of the structural adjustment required in the reactants prior to ET. The polarity of the surrounding medium is also important. If the ET reaction occurs in a medium containing mobile dipoles and/or ions, charge transfer will be accompanied by significant dipole and charge reorganisation. Where ET occurs over a long range (for example in the dye-sensitised solar cell), electron and ion motion may become coupled, because the energetic price paid for uncompensated charge separation is too great. That rapid progress that has been made in understanding all these factors over recent years owes much to theoreticians (aided by computational advances), and not a little to experimentalists (aided by ultrafast techniques) who have synthesised and investigated an armoury of increasingly sophisticated D–A and D–B–A ensembles.

Many individuals have contributed to ET rate theory, but in the context of photoconversion particular significance attaches to the work of Rudy Marcus of the California Institute of Technology, co-recipient of the 1992 Nobel Prize for chemistry, for it was he who first predicted the existence of the inverted region. In this chapter, after a historical survey of the field, we examine the classical Marcus theory of electron transfer, semiclassical and quantum-mechanical theories of nonadiabatic ET, and the adaptation of these theories to ET at electrodes. Our objective is to gain insight into good design features in photoconversion systems based on molecular chromophores and PET/ET reactions, whether in homogeneous or heterogeneous environments.

The importance of the ET field is attested by its abundant literature. ET and PET are comprehensively covered in book series edited by Jortner and Bixon (1999) and Fox and Chanon (1988), and more briefly by Grätzel (1989). Among reviews of ET theory, those of Norman Sutin and co-workers (Sutin, 1983; Sutin and Creutz, 1983; Newton and Sutin, 1984; Marcus and Sutin, 1985; Brunschwig and Sutin, 1999) are particularly helpful. Other general and more specialised accounts are provided by Meyer (1983),

Marcus and Sumi (1986), Ebersson (1987), McLendon (1988), Bolton and Archer (1991), Newton (1991, 1997), Meyer and Newton (1993), Bixon and Jortner (1997), Marcus (1997), Newton and Cave (1997), Chen and Meyer (1998), Hush (1999) and Newton *et al.* (1999). Adams *et al.* (2003) have reviewed charge transfer on the nanoscale.

4.2 Historical perspective

Electron-transfer reactions are unusual in that they can occur over 'long' edge-to-edge D–A distances (up to ~ 15 Å) that preclude collision. In outer-sphere ET reactions, no chemical bonds are made or broken, and no atom moves very far, although the nuclear configuration of the system does change in response to the movement of charge, in accordance with the Franck–Condon principle. This principle, developed in the mid-twenties to account for preferred vibronic transitions within molecules, states that the electron moves so rapidly compared with the more massive nuclei that electron transfer must occur at constant nuclear configuration. This principle was quickly recognised by Franck himself to apply equally to PET and ET reactions (Franck and Haber, 1931).

Given that there are differences in structure and solvation between the reactants and products of most electron-transfer reactions in condensed phases, the question then arose, at what point along the reaction coordinate did the electron actually transfer? Libby (1952), following Franck's own view, proposed that all the reorganisation took place after the electron step itself, following the Franck–Condon path marked *L* in Fig. 4.2. The greater the structural difference between R^0 and P^0 , the greater the energy required for step *L* and the slower the rate of ET. However, it was not clear how, in a thermal process, the reactants could obtain the high activation energy needed for step *L*, which is in effect a charge-transfer transition.

It was quickly recognised that there is a much lower energy route from the *R* to the *P* surface than path *L*, namely path *M* in Fig. 4.2. This involves some prior reorganisation in the *R* complex, taking it from its equilibrium configuration R^0 to the transition-state configuration $\ddagger$, where the electron can move from the *R* to the *P* surface in conformity with the Franck–Condon principle, and subsequent relaxation of the *P* complex from the strained configuration $\ddagger$ to its equilibrium configuration P^0 . The classical treatment of this reaction path was developed by Marcus (1956, 1959, 1960, 1964, 1965 and 1982) and Hush (1961, 1967, 1968), in a series of papers covering electrochemical and photo-induced electron transfer as well as thermal reactions. Reynolds and Lumry (1966) and Taube (1970) provided early books covering various aspects of ET theory.

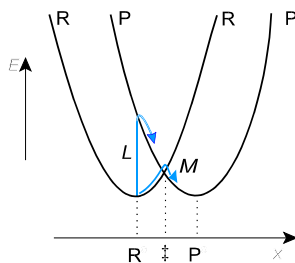


Figure 4.2 Section along the reaction coordinate X through the multidimensional potential energy surface of the ET reaction $D + A \rightleftharpoons D^+ + A^-$. R is the reactant complex (*i.e.* D and A at the reaction distance apart) and P is the product complex (*i.e.* D^+ and A^- at the same distance apart). R° and P° denote the equilibrium nuclear configurations of R and P, and $\ddagger$ is the transition-state configuration. L and M are the reaction paths suggested by Libby and Marcus respectively. This diagram is drawn for the case that R° and P° have the same energy, *i.e.* $\Delta G^\circ = 0$.

Out of classical Marcus theory came a compact expression of great power to rationalise the dependence of ET rates on the structure and solvation of the system. For both homogeneous and heterogeneous reactions, the rate constant k_{ET} could be expressed as

$$k_{\text{ET}} = A \exp \left[-\frac{(\lambda + \Delta G^\circ)^2}{4\lambda kT} \right] \quad (4.4)$$

where ΔG° is the free energy of reaction, λ is an important parameter known as the reorganisation energy, which is determined by the amount of structural reorganisation accompanying the reaction, and the prefactor A depends on the reaction type and the strength of the interaction between D and A. The inverted region occurs where $-\Delta G^\circ > \lambda$. In many systems, observation of the inverted region is masked by diffusion control, uncontrolled D–A distances or the formation of excited products, and its very existence remained controversial until the mid-eighties.

Beitz and Miller (1979) were the first to demonstrate the inverted region unequivocally, in their study of the transfer of trapped electrons to 48 different acceptors in a low-temperature glass. Figure 4.3, taken from their paper, shows the essentially parabolic dependence of $\ln k_{\text{ET}}$ on reaction driving force $-\Delta G^\circ$ predicted by eq. 4.4. Since then, ‘inverted’ rate behaviour has been confirmed in a wide range of D–A and D–B–A organic (*e.g.* Wasielewski *et al.*, 1985), inorganic/organometallic (*e.g.* Chen *et al.*, 1989) and biological (*e.g.* Moser *et al.*, 1992) supermolecules in homogeneous media. The observed dependence of k_{ET} on $-\Delta G^\circ$ is not, however, the symmetrical relation predicted by the classical relation, eq. 4.4. Instead the fall in the inverted region is usually slower than the rise in the normal region (Fig. 4.3 provides an example of this). This is because

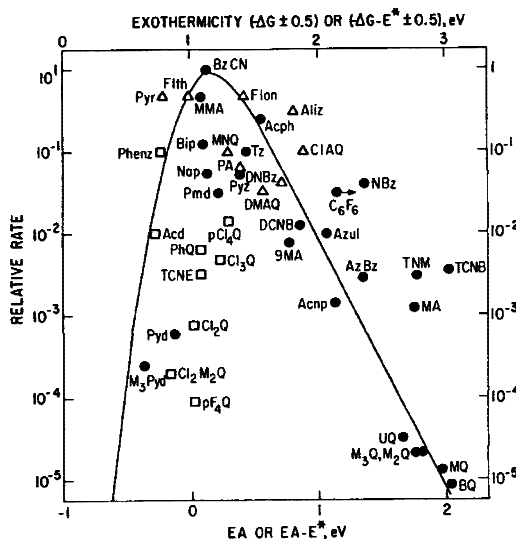


Figure 4.3 Relative rate constants for transfer of trapped electrons to various organic acceptors in glassy MTHF at 77 K. From Beitz and Miller (1979).

the quantisation of the vibrational modes of D and A is quite coarse, and this permits nuclear tunnelling (*i.e.* relaxation of the constraint of the Franck–Condon principle), particularly in the inverted region.

The classical theory developed by Marcus and Hush can offer no explanation for this, any more than it can for the occurrence of long-range ET, first observed in an ET protein by Chance and Nishimura (1960) and in a rigid glass by Miller (1975), or the sensitivity of ET rates to the nature of any molecules or molecular groups lying between the donor and acceptor, established by the pioneering work of Taube *et al.* (1953) and Taube and Myers (1954) on the inner-sphere ET reactions of transition-metal complexes.

Approaches beyond classical theory were clearly needed, and in the 1960s and 1970s two largely complementary quantum-mechanical approaches—the golden rule and superexchange—were developed. Modern computing power has essentially fused these two theories and greatly enhanced their reach and realism.

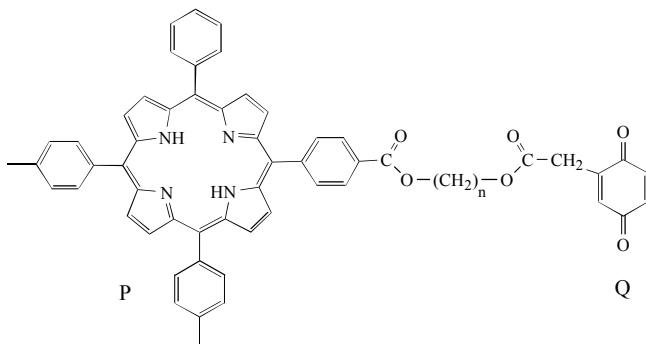
In the *golden rule* approach, developed by Jortner, Bixon and others (Kestner *et al.*, 1974; Ulstrup and Jortner, 1975; Jortner, 1976; Siders and Marcus, 1981a and 1981b; Bixon and Jortner, 1982), D and A are treated as weakly coupled but distinct entities and ET as a nonadiabatic radiationless transition between them governed by Fermi's golden rule, which may be written in the form

$$k_{\text{ET}} = \frac{2\pi}{\hbar} H_{\text{RP}}^2 \text{FCWD} \quad (4.5)$$

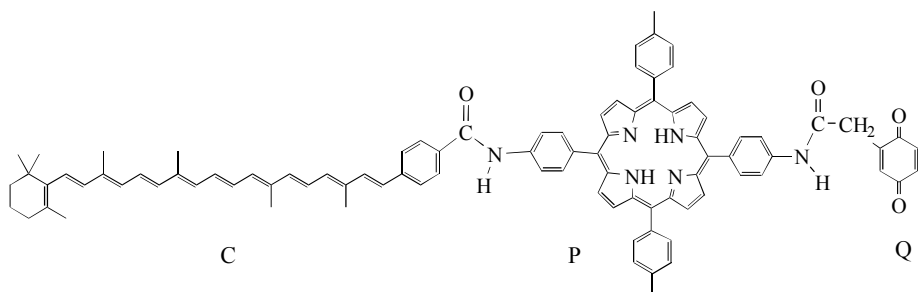
where H_{RP} is the matrix element coupling the R and P surfaces and allowing the electron to tunnel between the R and P surfaces, and FCWD is the Franck–Condon weighted density of states (see eq. 4.40), which is determined by the extent of nuclear reorganisation required to reach the transition state from the R^0 state. Expressions of this type were first applied to homogeneous ET by the Russian school (Levich and Dogonadze, 1959; Levich, 1965; Dogonadze *et al.*, 1972, 1973a, 1973b), and to electrochemical ET by Hush (1958, 1961), Gerischer (1970), Hale (1971) and Marcus (1975, 1977).

In the *superexchange* approach to nonadiabatic ET pioneered by Halpern and Orgel (1960) and McConnell (1961), the entire system, comprising D, A and the (linked or unlinked) medium or bridging groups B lying between them, is treated as a supermolecule D–B–A, *i.e.* an extended polyatomic molecule in which orbital overlap creates electron exchange interaction between D and A and enhances ET between them. McConnell's expression for the rate constant: $k_{ET} = A e^{-\beta l}$, where l is the bridge length and β an energy-dependent constant characteristic of the bridge and molecule, correctly predicted that superexchange rates would fall off exponentially with increasing bridge length. The theory of hopping conduction, the mechanism that takes over from superexchange in D–B–A supermolecules with longer bridges, was propounded by Miller and Abrahams (1960) and extended to variable-range hopping by Mott (1968).

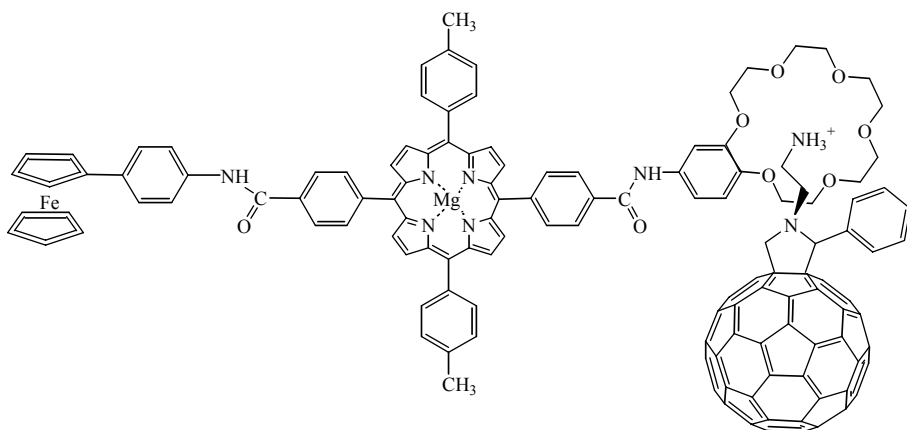
Photoconversion entered the story of ET in the 1970s, by which time knowledge of the structure and function of photosynthetic reaction centres was sufficient to allow the design and synthesis of 'dyads', D–A ensembles that held the donor and acceptor in well defined locations. The first DA dyads modelled on natural photosynthetic reaction centres were the porphyrin–quinone (P–Q) supermolecules of Kong and Loach (1978, 1980).



The first biomimetic triads were the P–Q–Q' compounds of Nishitani *et al.* (1983). In the carotenoid–porphyrin–quinone (C–P–Q) triad of Moore *et al.* (1984), shown on the next page,

COc1ccc(cc1)N2CCN(C2)c3ccc4c(=O)n(c5ccc6c(=O)n(c7ccc8c(=O)n(CCCCCC)cc87)c6=O)c5=O)c4=O

MeOAn-ANI-NI



Fc-MP-crown ether

Synthesis of covalently-linked polyads is a laborious task. An alternative approach is to create self-assembling supramolecular D:A ensembles, though it is challenging to create a single architecture if multiple equilibria may co-exist. D'Souza *et al.* (2006) adopted a hybrid approach by self-assembling an alkyammonium cation functionalised fullerene ($\text{NH}_3^+ - \text{C}_{60}$) with a covalently-linked ferrocene–porphyrin–crown ether (Fc–MP–crown ether) in the structure shown on the previous page. On excitation of the porphyrin donor, efficient forward electron transfer from MP to the fullerene acceptor, followed by hole transfer from MP^{++} to ferrocene, produced the final charge-separated state Fc⁺–MP–crown ether: $\text{NH}_3^+ - \text{C}_{60}$ with the impressive lifetime of 7.14 μs .

These *in vitro* endeavours in artificial photosynthesis have been greatly enriched and informed by the increased understanding of the *in vivo* photosynthetic process, following the seminal determination of the reaction centre structure of *R. spheroides* by Deisenhofer *et al.* (1984), and by studies of mutagenic and chemically engineered biological ET systems that now permit electron-transfer pathways and electronic couplings to be interrogated with exquisite precision.

4.3 Thermodynamics of ET and PET reactions

The free energy of reaction, ΔG° , is an important parameter in Marcus theory (as in, for example, eq. 4.4). Fortunately, this is an easy quantity to calculate from the redox potentials of the couples involved. For forward ET between ground-state D and A (eq. 4.1), the Nernst equation takes the form

$$\Delta G^\circ = -q(U_{\text{A},\text{A}^-}^\circ - U_{\text{D}^+,\text{D}}^\circ) \quad (4.6)$$

where $U_{\text{A},\text{A}^-}^\circ$ and $U_{\text{D}^+,\text{D}}^\circ$ are the standard reduction (redox) potentials of the D^+/D and A/A^- couples, on any convenient electrochemical scale. The condition for thermodynamically spontaneous reaction is that $\Delta G^\circ < 0$, *i.e.* that $U_{\text{A},\text{A}^-}^\circ > U_{\text{D}^+,\text{D}}^\circ$. The products D^+ and A^- are not then subject to back reaction, nor do they store energy. When reaction 4.1 is endergonic ($U_{\text{A},\text{A}^-}^\circ < U_{\text{D}^+,\text{D}}^\circ$), it cannot proceed far in the dark (unless the products are rapidly separated), and the back reaction (eq. 4.3) is thermodynamically spontaneous and typically fast. This is the case of most interest to us, for when the forward ground-state reaction is substantially ‘uphill’, its PET analogue



stores free energy that can be harnessed as work by the controlled recombination of D^+ and A^- , for example through an external electrical circuit.

The photoinduced electron transfer (PET) reaction 4.7 may follow excitation of D



or of A



or of a photosensitiser S, in which case S^* may either be reductively quenched by D, followed by regeneration of S by reaction of S^- with A



or oxidatively quenched by A, followed by regeneration of S by reaction of S^+ with D



In all cases, decay of the excited state (D^* , A^* or S^*) to the ground state may compete with electron transfer, and the PET reaction will only occur in good quantum yield if the ET rate is greater than the decay rate.

We can specify the conditions for the above sequences of reactions to be possible in terms of thermodynamic quantities provided we can ascribe these to electronically excited states. This is normally possible for excited states in bulk condensed phases because these become ‘thermalised’, *i.e.* vibrationally and rotationally equilibrated with their environment, extremely rapidly (usually within a few picoseconds), long before they undergo any chemical reaction. It is however not possible to assume thermalisation in space-quantised structures such as quantum dots, in which relatively long-lived hot carriers are generated by photoexcitation. Indeed, the very slowness of thermalisation in space-quantised structures makes it possible to envisage photoconversion devices in which hot carriers can deliver more work than would be thermodynamically possible with thermalised carriers. Nozik discusses such possibilities in Chapter 3.

Fully thermalised excited states may be treated as distinct chemical species with their own equilibrium thermodynamic properties, including redox potentials. We may therefore define standard redox potentials U_{D^+,D^*}^0 and U_{A^*,A^-}^0 for reactions of the excited states D^* and A^*



It is usually acceptable to assume that $\Delta V^0 = 0$ and $\Delta S^0 = 0$ for the excitation processes B.3 and B.5, and therefore that $\Delta G^0 = \Delta E^0$ for these processes. This is equivalent to assuming that the ground and excited states have very similar configurations and solvent environments, so the partition functions of the two states are the same. If the excited state is distorted with respect to the ground state, E_{00} in eqs. 4.18 and 4.19 should be replaced by the Gibbs energy of excitation, $\Delta G_{00} = E_{00} - T\Delta S_{00}$, where the entropy of excitation ΔS_{00} is calculated from the difference in configuration between the ground-state and excited chromophores. The internal energy change of the excitation can be obtained from the overlap of the absorption and fluorescence spectra as the 0–0 excitation energy ΔE_{00} .

The redox potentials of the excited-state and ground-state molecules can then be related by (Rehm and Weller, 1969) U

$$U_{D^+,D^*}^0 = U_{D^+,D}^0 - E_{00}^D/q \quad (4.20)$$

$$U_{A^*,A^-}^0 = U_{A^-,A}^0 + E_{00}^A/q \quad (4.21)$$

The redox potentials are expressed in volts. If the excitation energies E_{00}^D and E_{00}^A are expressed in electronvolts, the electronic charge $q = 1$ and its symbol is often omitted in eqs. 4.20 and 4.21. The bandgap energies usually lie in the range 1.8–3.2 V, so excitation transforms the redox potency of a chromophore.

These equations show that an excited state is both a much stronger oxidising agent and a much stronger reducing agent than the corresponding ground state. This is illustrated in Fig. 4.4. Excitation of an electron from the HOMO to the LUMO of the photosensitiser S places a high-energy electron (a strongly reducing species) in the LUMO and a high-energy hole (a strongly oxidising species) in the HOMO. If energy storage is to be achieved by oxidative quenching of D^* by A, reactions 4.9 and 4.11 must both be exergonic, so the redox potentials must fall in the order shown in Fig. 4.5a

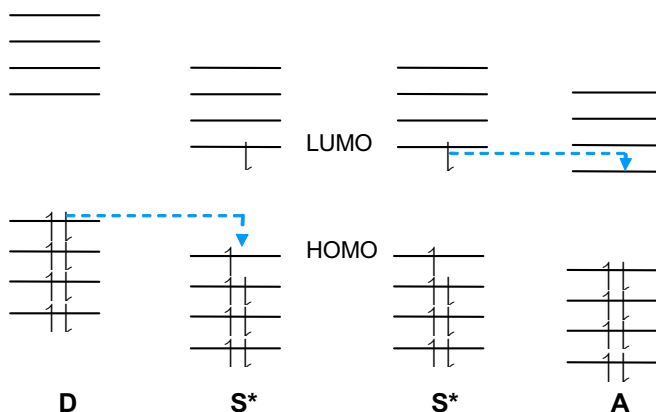


Figure 4.4 Molecular orbital diagram showing the HOMO (highest occupied molecular orbital) and LUMO (lowest occupied molecular orbital) of an excited sensitizer S^* . S^* can act as an oxidising agent if a suitable donor D is available, and as a reducing agent if a suitable acceptor A is available.

$$U_{D^+,D}^o > U_{A,A^-}^o > U_{D^+,D^*}^o \quad (4.22)$$

Similarly for reductive quenching of A^* by D , the redox potentials must fall in the order shown in Fig. 4.5b

$$U_{A^*,A^-}^o > U_{D^+,D}^o > U_{A^*,A}^o \quad (4.23)$$

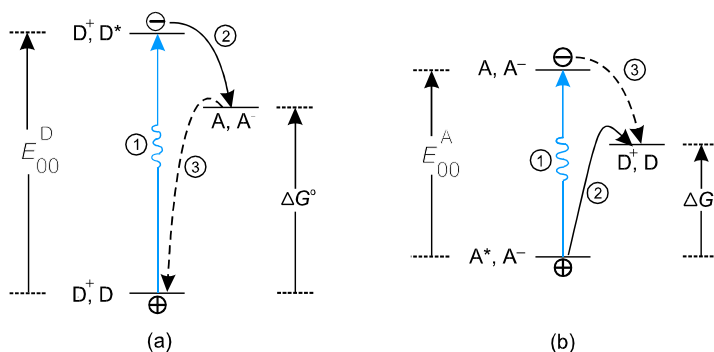


Figure 4.5 (a) Oxidative quenching of D^* by A ; (b) reductive quenching of A^* by D . The free energy stored in D^+ and A^- by the PET reaction is ΔG^o .

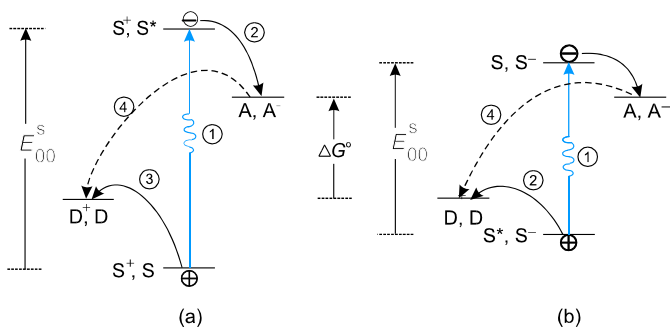


Figure 4.6 (a) Oxidative quenching of S* by A; (b) reductive quenching of S* by D.

For the sensitised reaction scheme 4.12–4.14, the sequence must be as in Fig. 4.6a

$$U_{S^*,S^-}^0 > U_{D^+,D}^0 > U_{A,A^-}^0 > U_{S,S^-}^0 \quad (4.24)$$

and similarly for scheme 4.15–4.17, the sequence must be as in Fig. 4.6b.

$$U_{S^+,S}^0 > U_{D^+,D}^0 > U_{A,A^-}^0 > U_{S^+,S^*}^0 \quad (4.25)$$

To determine the energy storage capability of a PET reaction involving thermalised excited states, we therefore need know only the chromophore excitation energy of the chromophore and the ground-state redox potentials of the two couples. The former can be estimated from the absorption spectrum of the chromophore or the overlap between its absorption and fluorescence spectra, if observable. The redox potentials are usually measured by an electrochemical technique such as cyclic voltammetry, though some correction may be necessary because electrochemistry generates DA^- or D^+A whereas light generates D^+A^- . The free energy of reaction used in Marcus equations such as eq. 4.4 should be corrected for any such effects, using the equation

$$\Delta G^0 = \Delta G^{0'} + w^p - w^R \quad (4.26)$$

where the uncorrected value $\Delta G^{0'}$ comes from electrochemical measurement (eq. 4.6), and w^R and w^p are the work of bringing D and A, and D^+ and A^- , respectively, from an infinite distance apart to the position where they react. These work terms can be quite significant where coulombic interaction between small charged moieties is involved, and calculating them can be the weakest link in understanding the reaction energetics.

Electron spin changes can also affect the thermodynamics (and kinetics) of ET. Most ET reactions occur without change of spin.² If D and A are both ground-state singlets, the radical-ion-pair (RIP) state D^+A^- formed by thermal ET is also a singlet. Similarly in PET reactions, if the excited chromophore and its reaction partner are both singlets, the RIP state is also a singlet, $^1(D^+A^-)$. However, if the singlet chromophore crosses to the triplet state and then reacts with a singlet reaction partner (e.g. if $^3D^*$ reacts with 1A), then the initially formed RIP state will also be a triplet, $^3(D^+A^-)$. The triplet RIP state lies below the singlet RIP state in energy, by an amount known as the singlet–triplet splitting. The magnitude of this depends on the coupling between the two unpaired electrons and the distance between D and A. In typical D–A supermolecules, the initial RIP spin state will dephase, typically on a nanosecond timescale, by hyperfine interactions with nearby magnetic nuclei, creating a statistical 1:3 mixture of singlet and triplet RIP states. The singlet phase will be the conduit for back reaction to ground-state D + A, since this is a spin-allowed process. The triplet RIP state should back-react more slowly (although the factors that permitted $^3D^*$ to form by intersystem crossing in the first place will also facilitate reverse intersystem crossing of $^3(D^+A^-)$ to the ground-state singlet DA manifold).

4.4 Classical Marcus theory

We now turn to the hierarchy of electron-transfer rate theories that have developed since the 1950s, starting with classical Marcus theory of homogeneous reactions and the development of eq. 4.4. In later sections we shall consider theories of nonadiabatic ET, which allow the identification and evaluation of the prefactor A in eq. 4.4, and also electrochemical ET, which differs from homogeneous reactions in that an electronic conductor is one of the ‘reactants’.

At the outset it is worth saying that although ET theories are naturally concerned with what governs the rate of the ET process itself, a preceding or (more rarely) a following step may be rate-determining for the overall process. For example, diffusion may limit the rate of bimolecular ET in homogeneous solution and also reaction at an electrode of a redox species in solution. In order to consider the rate of the ET step itself, free from the influence of any extrinsic dynamic bottlenecks, the *reactant* or *precursor complex*, denoted R, is usually taken as the starting point. This comprises the electron donor D and acceptor A, sited at the reaction distance apart, plus the surrounding medium falling

² ET reactions of transition metal complexes, where ligand-field effects can coerce a change from the low-spin to the high-spin configuration on change of redox state, are an exception.

under their influence. Any prior step such as diffusion needed to position D and A for reaction has already been accomplished in R. Similarly, the ‘end point’ of the ET step is taken to be the *product* or *successor complex*, denoted P, which comprises the products D^+ and A^- at the same distance apart as in R, plus the surrounding medium. The ET reaction can then be represented as



where R^o and P^o represent R and P in their equilibrium states. If necessary, the rates of formation and dissociation of the R^o and P^o complexes, by diffusion or other means, can be factored into the expression for the overall reaction rate (Marcus and Sutin, 1985) although, as it happens, many of the systems of interest in photoconversion incorporate D–A pairs localised in designed positions by a molecular bridge or a rigid matrix so that such steps are avoided.

4.4.1 The energy surface for reaction

The first stage in the calculation of k_{ET} is the construction of the multidimensional potential-energy surface for the reaction, since this enables the energy of activation to be obtained from *a priori* theoretical considerations. Figure 4.7 shows the energy surface for eq. 4.27 in the form of a contour diagram. R^o and P^o lie at energy minima in the R and P regions of the surface, respectively. The distortion coordinates 1 and 2 contain the nuclear coordinates of D and A, and those of the surrounding medium. The main response of the surrounding medium to the ET reaction is usually a change in its state of polarisation in response to the shift in charge. Often any specific, short-range solute–solvent interactions are ignored and the medium is treated as a structureless dielectric continuum. Its nuclear coordinates are then replaced by polarisation parameters.

The R and P surfaces intersect along a ‘ridge’, at each point of which the nuclear configurations and energies of R and P are necessarily the same.³ The reaction proceeds along the reaction coordinate X by the ascent of the system from R^o up to the lowest energy point on this ridge, which is the transition state marked ‡ in Fig. 4.7, and subsequent descent to P^o . X may be regarded simply as a suitably weighted nuclear position coordinate but, more generally, it is defined as the potential-energy difference

³ In the classical description of this section, we ignore both the coupling of the R and P states (which causes the R and P surfaces to split where they would otherwise cross) and the possibility of nuclear tunnelling from one surface to the other through the intervening energy barrier rather than passage over the barrier. These effects are considered in the next section.

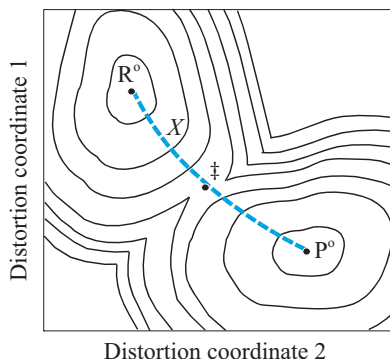


Figure 4.7 Schematic contour of the energy surface for the ET reaction $R^\circ \rightarrow P^\circ$. The blue dashed line is the nuclear coordinate X , and $\ddagger$ is the transition state.

between the R and P surfaces, all configurations with the same potential-energy difference having the same value of X . Any property that is directly proportional to this potential-energy difference may also be taken as the reaction coordinate (Hwang and Warshel, 1987; King and Warshel, 1990). R is in a state of constant thermal fluctuation, and electron transfer becomes possible (though by no means inevitable) when thermally activated fluctuations take R to the transition-state configuration $\ddagger$.⁴ The transferring electron can then cross rapidly from the R to the P surface in an isoenergetic event (the crossing probability depends on the extent to which the R and P states are mixed). During the crossing, the nuclei can barely move because they are much heavier than the electron. The Born–Oppenheimer principle therefore applies: the electron must transfer within a fixed nuclear framework. This rule applies rigorously within the constraints of classical theory, but is somewhat relaxed in semiclassical and quantum-mechanical treatments, which allow nuclei to move short distances by tunnelling between quantised modes of R and P.

The thermal fluctuations that take R° to the transition-state configuration are dominated by the internal vibrations of D and A and sympathetic adjustments in the state of polarisation of the surrounding medium. These both have a roughly harmonic effect on the energy of the system, that is, the energy in each mode varies roughly as the square of its displacement from equilibrium. Thus the R° and P° minima in Fig. 4.7 are depicted

⁴ In this classical description, we ignore both the coupling of the R and P states (which causes the R and P surfaces to split where they would otherwise cross) and the possibility of nuclear tunnelling from one surface to the other through the intervening energy barrier rather than passage over the barrier. These effects are considered in the next section.

as roughly, but by no means rigorously, paraboloidal depressions in the energy surfaces of R and P, with different curvatures for each along different coordinates.

Ab initio construction of such anharmonic energy surfaces for quite complicated systems has been feasible for some years, thanks to increased computing power and very time-efficient quantum-mechanical software. Many years before such calculations became possible, however, Marcus (1959, 1960, 1965) showed that, by treating the internal vibrational modes of D and D⁺, and A and A⁺, as symmetrised classical harmonic oscillators, and the surrounding medium as a structureless dielectric continuum whose polarisation responds linearly to charge, these roughly paraboloidal R and P surfaces were transformed to strictly paraboloidal free-energy surfaces of the same curvature in all dimensions. The variation in the free energy of R and P along the reaction coordinate *X* could then be represented in two-dimensional space simply as two parabolas of equal curvature intersecting at the transition state, as shown in Fig. 4.8. These parabolas are displaced vertically from each other by the free energy of reaction $-\Delta G^\circ$, and horizontally according to the extent of configurational change involved in the reaction $R^\circ \rightarrow P^\circ$.

Also shown in Fig. 4.8 is the important quantity known as the reorganisation energy λ of the reaction. This may be defined as the work required to distort the R complex from its equilibrium configuration R° to the equilibrium configuration P° of the P complex, but without transferring the electron (or equally as the work to distort P° to the configuration of R° but without transferring the electron). In terms of the Marcus diagram of Fig. 4.8, this can be identified as the vertical free-energy difference between R° and the point on the R parabola lying vertically above P° . Methods for evaluating λ are discussed in Section 4.4.3.

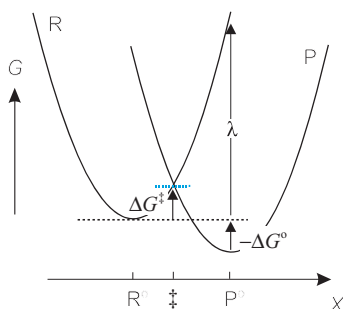
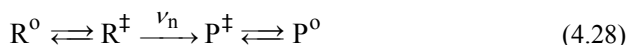


Figure 4.8 Classical Marcus theory section across the reaction coordinate *X* through the free energy hypersurface of the reaction complex R and product complex P for an ET reaction, showing the activation barrier $\Delta G^\ddagger$, the reorganisation energy λ and the free energy of reaction ΔG° .

4.4.2 The rate expression

The time scale of all except the very fastest ET and PET reactions is long compared with that required for thermal equilibration of the reactants with their surroundings. We can therefore apply transition-state theory and expand scheme 4.27 as



where the transition-state complex $R^\ddagger$, created by rapid thermal fluctuations in R , is taken to be in virtual equilibrium with R^o . The rate-determining step is passage through the transition-state region to form $P^\ddagger$ at the rate ν_n ; this rate may be dominated by a particular vibrational mode of R or the solvent or it may be a composite motion. In the classical (low-frequency, high-temperature) limit, ν_n takes the value kT/h ($\approx 10^{13} \text{ s}^{-1}$). The rate constant for reaction 4.27 may then be written⁵

$$k_{\text{ET}} = \kappa_{\text{el}} \nu_{\text{el}} K^\ddagger = \kappa_{\text{el}} \nu_{\text{el}} \exp(-\Delta G^\ddagger/kT) \quad (4.29)$$

where κ_{el} is the electronic transmission factor, that is, the fraction of $R^\ddagger$ that forms $P^\ddagger$. For adiabatic reactions (between strongly coupled donors and acceptors), $\kappa_{\text{el}} = 1$; for non-adiabatic reactions (between very weakly coupled donors and acceptors), $\kappa_{\text{el}} \ll 1$. $K^\ddagger$ is the ‘equilibrium constant’ for the pre-equilibrium $R^o \rightleftharpoons R^\ddagger$ (excluding the degree of freedom represented by ν_n), and $\Delta G^\ddagger$ is the standard free energy of activation, which is the vertical energy difference between R^o and $R^\ddagger$ in Fig. 4.8.

From the geometric properties of parabolas, it is easy to show that λ and ΔG^o are related by

$$\Delta G^\ddagger = (\lambda + \Delta G^o)^2/4\lambda \quad (4.30)$$

where ΔG^o is the standard free energy of reaction. Equation 4.30 is an example of a quadratic free energy relation. Unlike older (and theoretically less secure) linear free energy relations of the type $\Delta G^\ddagger = \beta + \alpha \Delta G^o$, where β and α are constants ($0 < \alpha < 1$), which predict that reaction rates will always rise as the driving force $-\Delta G^o$ for the reaction increases, eq. 4.30 predicts that the ET rate will rise to a maximum as $-\Delta G^o$ increases to the value λ , and fall thereafter. Combining eqs. 4.29 and 4.30, we obtain the *classical Marcus equation*

⁵ Equation 4.29 is valid for a reaction of any order provided that any concentration units incorporated in k_{ET} and $K^\ddagger$ are the same as those defining the standard states of the reactants and products in $\Delta G^\ddagger$.

$$k_{\text{ET}} = \kappa_{\text{el}} \nu_{\text{el}} \exp \left[-\frac{(\lambda + \Delta G^\circ)^2}{4\lambda kT} \right] \quad (4.31)$$

which predicts that $\ln k_{\text{ET}}$ will vary parabolically with $-\Delta G^\circ$ as shown in Fig. 4.9. The region where $-\Delta G^\circ < \lambda$, in which k_{ET} increases with $-\Delta G^\circ$, is known as the *normal region*, and the region where $-\Delta G^\circ > \lambda$ as the *inverted region*.

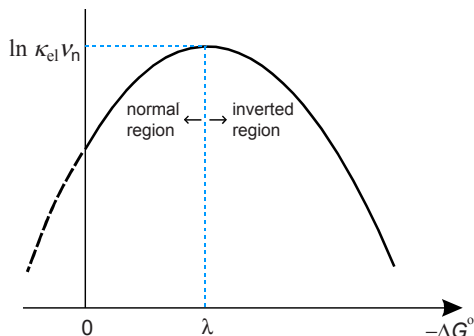


Figure 4.9 Variation of $\ln k_{\text{ET}}$ with $-\Delta G^\circ$ predicted by the classical Marcus expression, eq. 4.31. The maximum rate $\kappa_{\text{el}} \nu_n$ is attained when $\Delta G^\circ = -\lambda$. Where this maximum is high, the rate remains high over a range of ΔG° values, and can be substantial even for endergonic reactions (shown by the dashed line).

Reactions of the same λ but different ΔG° are represented by moving the P parabola vertically with respect to the R parabola, as shown in Fig. 4.10. For an isoenergetic reaction such as a self-exchange reaction, for which $\Delta G^\circ = 0$, it follows from eq. 4.31 that $\Delta G^\ddagger = \lambda/4$ (this case is shown in Fig. 4.10a). For moderately exergonic reactions, $\Delta G^\ddagger$ decreases and k_{ET} increases as ΔG° becomes increasingly negative in the normal region (Fig. 4.10b). When $-\Delta G^\circ = \lambda$ (Fig. 4.10c), the reaction can cross from the R to the P surface without prior distortion of R° and, from eq. 4.31, the rate constant then attains its maximum value of $\kappa_{\text{el}} \nu_n$. Thereafter, as ΔG° becomes ever more negative in a highly exergonic reaction (Fig. 4.10d), $\Delta G^\ddagger$ increases and $\ln k_{\text{ET}}$ decreases in the inverted region. Here the intersection of the R and P surfaces has moved to the left of the R° minimum. Physically this means that the reactants must become increasingly distorted to reach the transition state.

PET reactions can also be represented by Marcus parabolas. The R parabola for a PET reaction involving a thermalised excited state of D or A is simply related to that of the

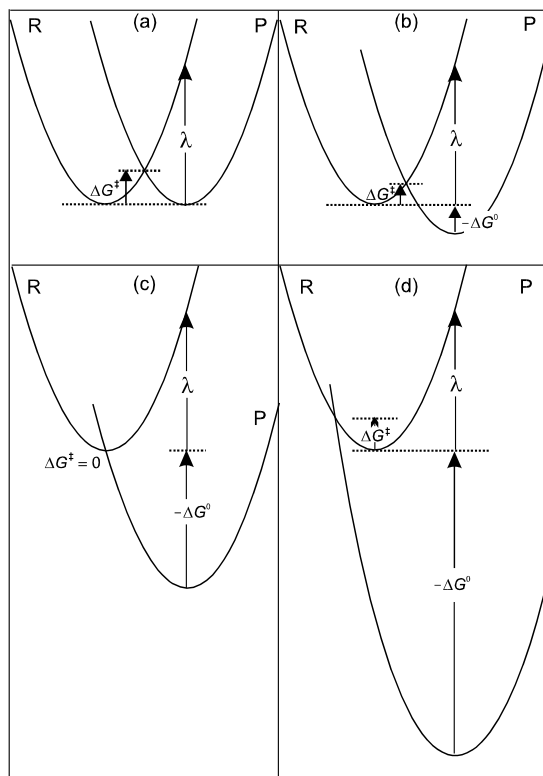


Figure 4.10 Free energy profiles along the reaction coordinate for: (a) a reaction of zero $-\Delta G^\circ$; (b) the normal region where $0 \leq -\Delta G^\circ \leq \lambda$; (c) the condition for maximum rate constant where $-\Delta G^\circ = \lambda$; (d) the inverted region where $-\Delta G^\circ > \lambda$.

corresponding ground-state ET reaction: the R parabola is shifted vertically upwards with respect to the P parabola by the excitation energy E_{00} of the chromophore, and horizontally along the reaction coordinate if there is any difference in geometry between the ground and excited state of the chromophore that is manifest in this coordinate. The vertical transition transforms the reaction energetics (an example is shown later, in Fig. 4.28) and makes many energy-storing PET reactions possible.

The classical Marcus expression, eq. 4.31, has its limitations exactly because it is classical. It also has great strengths. It predicts the inverted region. It provides a powerful physical model of ET (and PET), which will enable us to draw inferences about optimal conditions for PET in Section 4.9. It also indicates that varying the medium (and hence λ) for a reaction of given $-\Delta G^\circ$ will markedly change k_{ET} . A reaction with small $-\Delta G^\circ$

will run fastest in a medium of low polarity with a matched low value of λ . Running the same reaction in a medium of high polarity could easily, according to eq. 4.31, reduce k_{ET} by a factor of up to $\sim 10^4$ (though it will also stabilise the charge-separated state D^+A^- with respect to back ET via the excited state). A reaction with high $-\Delta G^\circ$ will run fastest in a medium of high polarity, and reducing the polarity will, according to eq. 4.31, reduce k_{ET} even more strongly. However, this takes the system into the inverted region, where the classical model underestimates ET rates because it ignores nuclear tunnelling. Nevertheless, it is clear that manipulating the medium can make a substantial contribution to the control of ET rates.

4.4.3 The reorganisation energy

An important aspect of Marcus's early work was his treatment of the reorganisation energy λ . This he took as the sum of two contributions, the *inner reorganisation energy* λ_{in} and the *outer or solvent reorganisation energy* λ_{out} .

$$\lambda = \lambda_{\text{in}} + \lambda_{\text{out}} \quad (4.32)$$

The inner term λ_{in} is the work required to reorganise D and A (but not the surrounding medium) from the nuclear configurations of R° to those of P° . Marcus treated the vibrations of D and A as classical (that is, non-quantised) harmonic oscillations with symmetrised force constants. (This symmetrisation is a necessary part of making the curvatures of the R and P parabolas equal.)

For the self-exchange reaction $\text{D}^+ + \text{D} \rightleftharpoons \text{D} + \text{D}^+$ in a homogeneous medium, the symmetrised inner reorganisation energy $\lambda_{\text{in}}^{\text{D}^+, \text{D}}$ is calculated as

$$\lambda_{\text{in}}^{\text{D}^+, \text{D}} = \sum_j \frac{f_j^{\text{D}^+} f_j^{\text{D}}}{f_j^{\text{D}^+} + f_j^{\text{D}}} (\Delta x_j^\circ)^2 \quad (4.33)$$

where f_j^{D} and $f_j^{\text{D}^+}$ are the force constants of the j th normal vibrational mode in D and D^+ , and Δx_j° is the amount by which the equilibrium value of the j th normal coordinate differs in D and D^+ .

The inner reorganisation energy $\lambda_{\text{in}}^{\text{A}, \text{A}^-}$ for the $(\text{A} + \text{A}^-)$ self-exchange reaction is similarly calculated over all normal modes i of A as

$$\lambda_{\text{in}}^{\text{A}, \text{A}^-} = \sum_i \frac{f_i^{\text{A}} f_i^{\text{A}^-}}{f_i^{\text{A}} + f_i^{\text{A}^-}} (\Delta x_i^\circ)^2 \quad (4.34)$$

The inner reorganisation energy $\lambda_{\text{in}}^{\text{D,A}}$ for the cross-exchange ET reaction between D and A in homogeneous solution is then obtained additively as

$$\lambda_{\text{in}}^{\text{D,A}} = \frac{1}{2}(\lambda_{\text{in}}^{\text{D}^+, \text{D}} + \lambda_{\text{in}}^{\text{A}, \text{A}^-}) \quad (4.35)$$

where the factor of $\frac{1}{2}$ appears because two D^+/D or A/A^- couples are involved in each self-exchange reaction, but only one in the cross-exchange reaction. The calculation of $\lambda_{\text{in}}^{\text{D,A}}$ requires knowledge of the vibration frequencies and geometries of D, D^+ , A and A^- . Where the structural differences between the reactants and products are modest, $\lambda_{\text{in}}^{\text{D,A}}$ is also modest, typically < 0.3 eV.

The solvent reorganisation energy λ_{out} in eq. 4.32 is the work required to transform the medium around the reactants from its configuration in R^0 to that in P^0 . Regarding the solvent as structureless dielectric continuum, these solvent configurations differ because the equilibrium state of polarisation of the medium around the reactants, D and A and the products, D^+ and A^- , with their necessarily different charges, are different. Provided that solvent polarisation responds linearly to solute charge,⁶ λ_{out} can be calculated as

$$\lambda_{\text{out}} = \frac{\epsilon_0}{2} \left[\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_{\text{s}}} \right] \int (\mathcal{E}^{\text{R}} - \mathcal{E}^{\text{P}})^2 dV \quad (4.36)$$

where $\mathcal{E}^{\text{R}}$ and $\mathcal{E}^{\text{P}}$ are the electric fields exerted *in vacuo* by R and P, ϵ_{op} and ϵ_{s} are the optical and static dielectric constants of the solvent, and the integral is taken over the volume V . Equation 4.36 expresses the difference between the work of transforming the solvent from its state of polarisation in R^0 to that in P^0 slowly, so that the electronic, nuclear and orientational components of the polarisation all respond, and then very rapidly, so that only the electronic polarisation can respond.

Integration of eq. 4.36 requires a geometric model of R and P so that appropriate expressions for $\mathcal{E}^{\text{R}}$ and $\mathcal{E}^{\text{P}}$ can be chosen. If D and A are treated as spheres with point charges at their centres, integration yields

$$\lambda_{\text{out}} = \frac{(\Delta q)^2}{4\pi\epsilon_0} \left[\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_{\text{s}}} \right] \left[\frac{1}{2r_{\text{D}}} + \frac{1}{2r_{\text{A}}} - \frac{1}{r_{\text{DA}}} \right] \quad (4.37)$$

⁶ This is the other condition that must be fulfilled if the R and P parabolas are to have the same curvature. While it usually holds, nonlinear effects such as dielectric saturation are possible, and eq. 4.36 is then inapplicable.

where Δq is the charge transferred in the reaction (almost always one electronic charge because λ_{out} is prohibitively high for simultaneous two-electron transfers), r_{D} and r_{A} are the radii of D and A, including any ‘inner’ solvent shells that are counted as part of D and A, and r_{DA} is the centre-to-centre D–A distance in the reactant complex.

Equation 4.37 predicts that λ_{out} will vary from ~ 0.15 eV for non-polar solvents (for which ϵ_{s} is not much greater than ϵ_{op}) up to ~ 1.0 eV for highly polar solvents (for which $\epsilon_{\text{s}} \gg \epsilon_{\text{op}}$), reflecting the extensive solvent dipole reorientation that then accompanies the reaction. Usually λ_{out} dominates λ_{in} in determining the overall value of λ . Temperature also affects λ_{out} slightly through the temperature dependence of ϵ_{op} and ϵ_{s} , but usually by $< 5\%$ over a 100 K temperature range. Equation 4.37 also predicts that λ_{out} will vary with r_{DA} , tending to a constant value when $r_{\text{DA}} \gg (r_{\text{D}} + r_{\text{A}})$ and D and A are well separated, but decreasing at smaller r_{DA} to a minimum when D and A are in van der Waals contact and $r_{\text{DA}} = (r_{\text{D}} + r_{\text{A}})$. Physically, this is because the spheres of solvent polarisation around D and A increasingly interpenetrate as r_{DA} decreases, and thus extend over a smaller total volume. This distance effect on λ_{out} can be appreciable, up to a few tenths of an eV for small D and A in polar media, but otherwise it is modest. Nevertheless, we should note that λ_{out} , unlike λ_{in} , cannot be calculated as the sum of independent contributions from D and A, except in the limit that $r_{\text{DA}} \gg (r_{\text{A}} + r_{\text{D}})$.

Expressions for λ_{out} for other reactant geometries (Brunschwig *et al.*, 1986) and more complex electrostatic models have been given. Irrespective of the model chosen, it is usually possible to express λ_{out} as

$$\lambda_{\text{out}} = B \left[\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_{\text{s}}} \right] \quad (4.38)$$

where B is a solvent-independent parameter determined by the geometry of D and A. Measured values of λ_{out} are typically ~ 0.15 eV for aliphatic hydrocarbons, ~ 0.03 – 0.2 eV for membrane proteins and 0.5 – 1.0 eV for polar solvents.

4.5 Semiclassical theories of nonadiabatic electron transfer

The classical Marcus expression, eq. 4.31, assumes the internal modes of R and P to behave classically and is primarily aimed at adiabatic reactions with $\kappa_{\text{el}} = 1$, offering no method of evaluating $\kappa_{\text{el}} < 1$ for nonadiabatic transfer between more distant or weakly coupled donors and acceptors. This requires nonclassical approaches, to which we now turn. Semiclassical approaches, dealt with in this section, incorporate the quantisation of the internal modes of D and A but retain the classical treatment of the surrounding medium as a structureless dielectric continuum.

The usual starting point for calculating nonadiabatic ET rates within a nonclassical framework is Fermi's golden rule. This gives the rate constant k_i for crossing from the i th vibrational level of a reactant complex R to a set of levels j of a product complex P (where R and P are any two weakly coupled electronic states) as

$$k_i = \frac{2\pi}{\hbar} H_{\text{RP}}^2 \sum_j \langle \chi_{\text{P}j} | \chi_{\text{R}i} \rangle^2 \delta(\epsilon_{\text{P}j} - \epsilon_{\text{R}i}) \quad (4.39)$$

where $\chi_{\text{P}j}, \chi_{\text{R}i}$ are the wavefunctions, and $\epsilon_{\text{P}j}, \epsilon_{\text{R}i}$ the energies, of the states $\text{P}j$ and $\text{R}i$, δ is the Dirac delta function that ensures energy conservation ($\delta = 0$ if $\epsilon_{\text{P}j} \neq \epsilon_{\text{R}i}$; $\delta = 1$ if $\epsilon_{\text{P}j} = \epsilon_{\text{R}i}$), and the sum is taken over all vibrational states of P (including solvent oscillators) that have the same energy as $\text{R}i$.

Provided that vibrational relaxation and excitation are fast compared with the ET step so that the pre-equilibrium in scheme 4.28 is established, the overall rate constant for ET can be found by summing k_i over all vibrational levels i of R, each weighted by the Boltzmann probability $p(\epsilon_{\text{R}i})$ of its being occupied, giving

$$k_{\text{ET}} = \frac{2\pi}{\hbar} H_{\text{RP}}^2 \sum_i \sum_j \langle \chi_{\text{P}j} | \chi_{\text{R}i} \rangle^2 p(\epsilon_{\text{R}i}) \delta(\epsilon_{\text{P}j} - \epsilon_{\text{R}i}) \quad (4.40)$$

where

$$p(\epsilon_{\text{R}i}) = \frac{\exp(-\epsilon_{\text{R}i}/kT)}{\sum_i \exp(-\epsilon_{\text{R}i}/kT)} \quad (4.41)$$

The summed term in eq. 4.40 is often referred to as the Franck–Condon weighted density of states (FCWD), and the equation written in the compact form of eq. 4.5. This is the ‘master equation’ for the calculation of rates of nonadiabatic ET where the reactants remain in thermal equilibration with their surroundings.

4.5.1 Donor–acceptor coupling

A nonclassical theory of ET must take account of the interaction between the R and P states of the system. We noted, in connection with Figs. 4.7 and 4.8, that the R and P surfaces do not really cross unless the R and P states are diabatic (non-interacting). However, they must interact to some extent if ET is to be possible. This interaction mixes the R and P wavefunctions and creates an ‘avoided crossing’ in the intersection region with a vertical splitting between them of $2H_{\text{RP}}$, as shown in Fig. 4.11. The coupling matrix element (loosely, the D–A interaction energy) H_{RP} is calculated as

$$H_{\text{RP}} = \langle \psi_{\text{R}} | \hat{\mathcal{H}}_{\text{el}} | \psi_{\text{P}} \rangle \quad (4.42)$$

where H_{RP} is the electronic interaction Hamiltonian and ψ_{R} and ψ_{P} are the wavefunctions of the nonadiabatic R and P states, which differ mainly because the electron is localised on D in ψ_{R} , but on A in ψ_{P} . H_{RP} values can be inferred from spectroscopic data on charge-transfer transitions or calculated from the generalised Mulliken–Hush equations (Cave and Newton, 1996). Since ψ_{R} and ψ_{P} fall off exponentially in their tail regions, H_{RP} falls off exponentially with the distance r_{DA} between D and A. This is usually written as

$$H_{\text{RP}} = H_{\text{RP}}^{\circ} \exp[-(\beta/2)(r_{\text{DA}} - r_{\text{DA}}^{\circ})] \quad (4.43)$$

where H_{RP}° is the value of H_{RP} at the reference distance r_{DA}° (normally the edge-to-edge or centre-to-centre distance when D and A are in close contact) and β is the *attenuation coefficient* or *decay constant* for electron transfer.

Figure 4.11 shows the difference between nonadiabatic and adiabatic ET. When the interaction between R and P is very weak (Fig. 4.11a), H_{RP} is small. The reaction is then nonadiabatic, with electronic transmission coefficient $\kappa_{\text{el}} \ll 1$, because the system usually remains on the R surface as it fluctuates through the configuration $\text{R}^{\ddagger}$ rather than reacting by crossing to the P surface. When the coupling is strong, on the other hand (Fig. 4.11b), the reaction is adiabatic ($\kappa_{\text{el}} = 1$). The energy surfaces are well separated in the intersection region, so that every fluctuation of R that takes it to the configuration $\text{R}^{\ddagger}$ results in reaction along the lower energy surface.

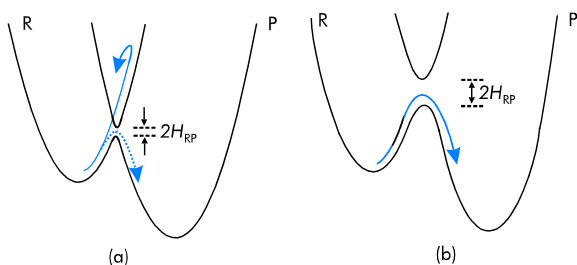


Figure 4.11 Free energy profiles and reaction trajectories for (a) nonadiabatic and (b) adiabatic electron transfer between R and P. H_{RP} is the electronic coupling matrix element.

The value of H_{RP} at which an electron transfer is to be regarded as adiabatic or nonadiabatic varies with the system, but the equality $H_{\text{RP}} \approx kT$ is a rough guide. Strongly adiabatic reactions have $H_{\text{RP}} > 0.025$ eV at room temperature and strongly nonadiabatic ones have $H_{\text{RP}} < 0.001$ eV. Nonadiabatic ET is likely where D and A are separated by distances large compared with their own sizes, for example in long-range biological ET

and in bridged D–A supermolecules where the bridge contains more than a few units. Adiabatic ET becomes likely where D and A are in close (van der Waals) contact or linked by a short bridge with strong coupling between the orbitals of D, A and the bridge. The couplings in a PET reaction may be stronger than in the equivalent thermal ET reaction because the LUMO of the excited chromophore is spatially more extended and diffuse than its HOMO. If the coupling becomes very strong ($H_{\text{RP}} \geq \lambda/2$), the electron is delocalised rather than being localised on D or A, and ET can no longer be regarded as occurring between two distinct states of the system.

4.5.2 Nuclear tunnelling

Another factor of which a nonclassical theory must take account is the quantisation of the internal modes of D and A, and the consequent relaxation of the Born–Oppenheimer constraint that the electron must transfer within a fixed nuclear framework. In classical theory, the vibrational modes of D and A are treated as classical harmonic oscillators, but in reality their quantisation is usually significant (that is, one or more of the vibration frequencies ν is sufficiently high that the classical limit $h\nu \ll kT$ does not apply). Electron transfer then requires the overlap, not only of the electronic wavefunctions of R and P, but also of their vibrational wavefunctions. It is then possible that nuclear tunnelling may assist electron transfer. As shown in Fig. 4.12, the vibrational wavefunctions of R and P extend beyond the classical parabolas and overlap to some extent. This permits nuclear tunnelling from the R to the P surface, particularly in the region just below the classical intersection point. Part of the reorganisation of D and A, required prior to ET in the classical picture, may then occur simultaneously with ET, by the nuclei tunnelling short (typically $< 0.1 \text{ \AA}$) distances from their R to their P positions.

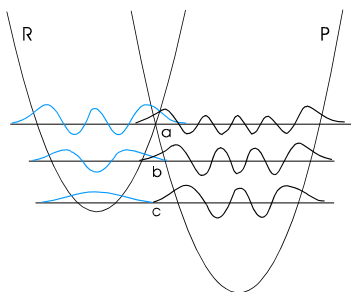


Figure 4.12 Potential energy diagram for the quantum-mechanical model of electron transfer. The vibrational wavefunctions of R (shown in blue) overlap with those of P and allow nuclear tunnelling.

Nuclear tunnelling enhances the ET rate by providing several parallel avenues for reaction. This may still occur at the classical crossing point (curve *a* in Fig. 4.12), by pure electron tunnelling preceded by thermally activated reorganisation to the classical transition state. But ET can also occur from vibrational levels of R below the classical intersection point, provided the surfaces remain close enough for nuclear tunnelling. When crossing takes place from a thermally activated state of R (as in curve *b*), ET still requires activation and the rate retains some temperature dependence. When nuclear tunnelling from the vibrationless state of R to the P surface is possible (curve *c*), the ET rate will show an activationless component that persists down to the lowest temperatures.

4.5.3 Semiclassical rate expressions

In semiclassical treatments (Kestner *et al.*, 1974; Ephrussi and Bixon, 1974) of ET, the ‘golden rule’ expression, eq. 4.40, is adapted to treat solvent modes classically and the internal modes quantum mechanically. This equation can then be rewritten as the *semiclassical Marcus equation* (Marcus and Sutin, 1985)

$$k_{\text{ET}} = \frac{2\pi}{\hbar} H_{\text{RP}}^2 (4\pi\lambda_{\text{out}} kT)^{-1/2} \sum_j \sum_i \langle \chi_{\text{Pj}} | \chi_{\text{Ri}} \rangle^2 p(\epsilon_{\text{Ri}}) \exp \left[-\frac{(\epsilon_{\text{Pj}} - \epsilon_{\text{Ri}} + \lambda_{\text{out}} + \Delta G^\circ)^2}{4\lambda_{\text{out}} kT} \right] \quad (4.44)$$

where λ_{out} is the classical solvent reorganisation energy calculated from eq. 4.37. This equation may be further simplified by representing the internal vibrations as a single mode of frequency ν (Ephrussi and Bixon, 1974; Ulstrup and Jortner, 1975), giving

$$k_{\text{ET}} = \frac{2\pi}{\hbar} H_{\text{RP}}^2 (4\pi\lambda_{\text{out}} kT)^{-1/2} \sum_{m=0}^{\infty} (e^{-S} S^m / m!) \exp \left[-\frac{(\Delta G^\circ + \lambda_{\text{out}} + m h \nu)^2}{4\lambda_{\text{out}} kT} \right] \quad (4.45)$$

where $S = \lambda_{\text{in}} / h \nu$. This expression maximises where $-\Delta G^\circ = \lambda_{\text{in}} + \lambda_{\text{out}} = \lambda$, as does the classical equation (eq. 4.31).

In the limit that $h \nu \gg kT$, eq. 4.45 reduces to the low-temperature *exponential energy-gap law* (Engelman and Jortner, 1970)

$$k_{\text{ET}} \propto \exp(-\gamma |\Delta E|/h\nu) \quad (4.46)$$

where ΔE is the internal energy change of the ET reaction, and γ is a numerical factor that depends weakly on ΔE . This low-temperature limiting value of k_{ET} is predicted to be independent of temperature but strongly dependent on ν .

In the limit that $h\nu \ll kT$, eq. 4.45 reduces to the *high-temperature limit semiclassical equation*

$$k_{\text{ET}} = \frac{2\pi}{\hbar} H_{\text{RP}}^2 (4\pi\lambda kT)^{-1/2} \exp\left[-\frac{(\lambda + \Delta G^\circ)^2}{4\lambda kT}\right] \quad (4.47)$$

This is perhaps the most commonly used equation for nonadiabatic ET. It retains the classical expression, $\exp[-(\lambda + \Delta G^\circ)^2/4\pi kT]$, for the nuclear reorganisation term, and identifies the electronic term $\kappa_{\text{el}}\nu_n$ of eq. 4.29 as

$$\kappa_{\text{el}}\nu_n = \frac{2\pi}{\hbar} H_{\text{RP}}^2 (4\pi\lambda kT)^{-1/2} \quad (4.48)$$

This is satisfactory in that eq. 4.48 is identical with the semiclassical Landau–Zener expression for the crossing probability between R and P surfaces of the same curvature in the weak-coupling limit (Newton, 1991).

The high-temperature semiclassical limit equation, eq. 4.47, and the single-frequency semiclassical equation, eq. 4.45, give closely similar results in the normal region

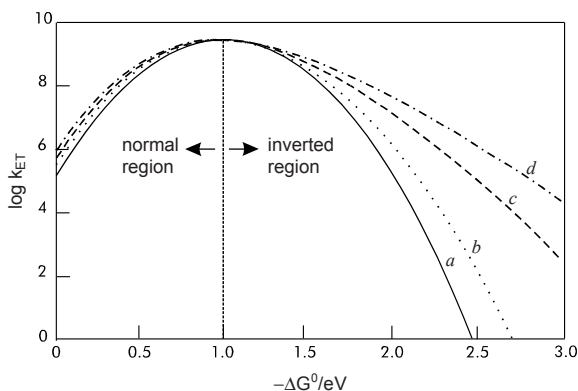


Figure 4.13 Variation of $\log k_{\text{ET}}$ with the free energy $-\Delta G^\circ$ of reaction. Curve *a* has been calculated from the high-temperature semiclassical limit eq. 4.47 with $\lambda_{\text{in}} = 0.20$ eV, $\lambda_{\text{out}} = 0.80$ eV, $T = 300$ K; curves *b*, *c* and *d* have been calculated from the single-frequency semiclassical expression eq. 4.45 with $\tilde{\nu} = \nu/c = 750$, 1500 and 2250 cm^{-1} , respectively.

($-\Delta G^\circ < \lambda$) and up to the Marcus maximum, where the single-frequency model also predicts a maximum. However, eq. 4.47 predicts that the fall-off in $\ln k_{\text{ET}}$ with $-\Delta G^\circ$ past the Marcus maximum will follow a classical parabola, as shown in curve *a* of Fig. 4.13, whereas eq. 4.45 predicts a more gradual fall-off, as shown in curves *b*, *c* and *d*, which is in much better accord with experimental observations (*e.g.* Fig. 4.3). This is because the high-frequency model permits crossing to excited vibronic states of P, and nuclear tunnelling to these is facilitated by the large Franck–Condon overlap of the embedded R and P vibrational wavefunctions in the inverted region, as shown in Fig. 4.14.

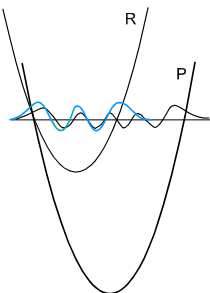


Figure 4.14 Embedded R and P vibrational wavefunctions in the inverted region, leading to facile nuclear tunnelling between the two states.

4.6 Electron transfer in donor–bridge–acceptor supermolecules

In many ET and PET reactions, the donor and acceptor are not in close contact but rather are separated by a ‘bridge’ of intervening molecular units. As noted in section 4.1, D and A may be covalently linked via a molecular bridge in a donor–bridge–acceptor (D–B–A) supermolecule, where B stands for one or more bridging units. Alternatively, D and A may be unconnected molecules separated by molecules of the surrounding medium or held at a fixed distance from each other in some sort of molecular cage. In either case, the orbitals of the intervening molecules may facilitate long-range electron transfer by one or more ‘through-bond’ pathways. As shown schematically in Fig. 4.15a, these pathways arise from the overlap of the frontier orbitals of neighbouring bridging groups with each other and with the frontier orbitals of the terminal D and A moieties. In ground-state ET/HT, the frontier orbitals are normally the HOMO of D and the LUMO of A. In PET reactions the LUMO of D* or the HOMO of A* becomes a frontier orbital; these are probably more extended in space than the corresponding HOMOs, which would facilitate the forward PET step. The effective coupling between D and A via the bridge is thereby

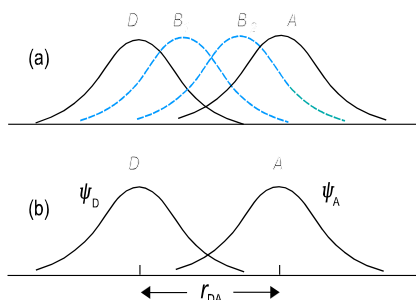


Figure 4.15 (a) Enhanced 'through-bond' overlap in DBA via the frontier orbitals of the bridging units (two in this example, shown in blue); (b) weaker 'through-space' overlap between the tails of the D and A wavefunctions ψ_D and ψ_A at the same D-A edge-to-edge distance r_{DA} .

much enhanced as compared with the 'through-space' overlap (Fig. 4.15b) that is the only possible mode of interaction between D and A in the absence of other molecules.

The mechanism of ET or HT depends on the relative energies of the frontier orbitals of D, A and the bridge, as shown in Fig. 4.16. Where the bridge frontier orbitals are considerably higher in energy than those of D or A, the operative mechanism is superexchange and the bridge orbitals participate only by means of the virtual states D^+B^-A (for ET) or DB^+A^- (for HT). Figure 4.16a illustrates the ET superexchange process. The electron passes from D to A without pausing on B for any meaningful length of time, and ET is a coherent process (meaning that the travelling electron wave remains in phase). The ET rate falls off exponentially with the D-A edge-to-edge distance.

When the frontier orbitals of the bridge are not much higher in energy than those of D (for ET) or A (for HT), the dominant mechanism becomes incoherent charge hopping. Figure 4.16b shows ET by this mechanism. The electron hops in a thermally activated step from D onto the bridge frontier orbital(s) before it comes to rest on A. The intermediate state D^+B^-A is populated and the electron phase coherence is lost. The

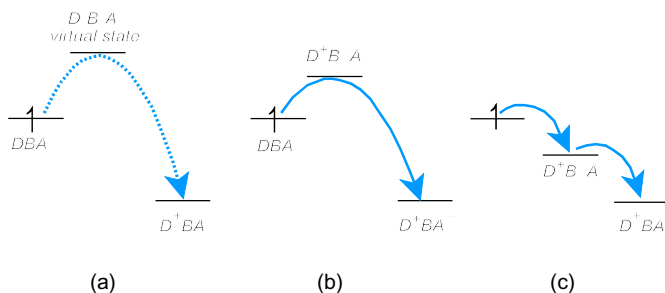


Figure 4.16 Electron transfer in DBA by (a) the superexchange mechanism; (b) charge hopping; (c) the sequential mechanism.

distance dependence of incoherent charge hopping depends on the extent of conjugation (*i.e.* charge delocalisation) in the bridge. Where the charge hops from one bridge unit to the next, the ET rate falls off linearly with the number of units in the bridge.

A third possibility is that the bridge orbitals are of lower energy than the frontier orbital of D, as shown in Fig. 4.16c, in which case D^+B^-A is a genuine chemical intermediate in the ET chain. However, D^+B^-A can form as a short-lived intermediate even where ET from D to B is endergonic; this occurs in natural oxoreductase proteins (Page *et al.*, 1999). Finally, if the frontier orbitals of D or A and the bridge are degenerate or nearly so, charge will delocalise onto the bridge, and *resonant tunnelling* can occur.

4.6.1 Superexchange

Superexchange is incorporated into nonadiabatic ET rate theory by reinterpreting the coupling element H_{RP} as the effective coupling element between D and A via the bridge. To emphasise this point, H_{RP} is often re-labelled and re-badged as the *transfer integral* T_{DA} in superexchange theory, and the ‘Fermi’s golden rule’ nonadiabatic rate equation (eq. 4.5) written in the form

$$k_{ET} = \frac{2\pi}{\hbar} T_{DA}^2 \text{FCWD} \quad (4.49)$$

FCWD is calculated, as usual, by calculating or measuring ΔG° and λ , or from a semiclassical expression such as eq. 4.44. The appropriate form for T_{DA} depends on what assumptions are made about the orbitals, couplings and allowed pathways involved in superexchange. Figure 4.17 shows the example of a supermolecule $DB_1B_2\dots B_{n-1}B_nA$, consisting of terminal D and A moieties singly connected by a bridge with n hetero-

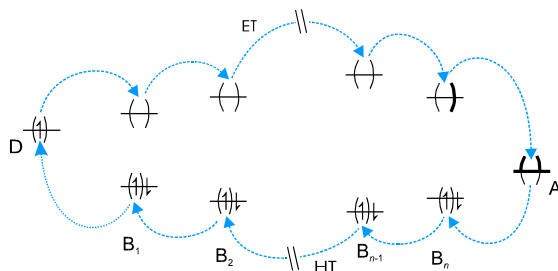


Figure 4.17 Schematic representation of bridge-mediated electron transfer (ET) and hole transfer (HT) in a linear $DB_1B_2\dots B_{n-1}B_nA$ supermolecule. The dominant route (ET or HT) involves the bridge orbitals lying nearer in energy to the frontier orbitals of D and A.

geneous units, in which ET from D to A is assumed to occur in the forward-only direction, and the tight-bonding assumption that only nearest-neighbour interactions are important is made. In this case, for ET via the bridge LUMOs, T_{DA} is given by (Larsson, 1981; Ratner, 1990)

$$|T_{DA}| = (H_{DB_1}/\Delta E_{DB_1}) \left[\prod_{i=1}^{n-1} (H_{B_i B_{i+1}}/\Delta E_{DB_{i+1}}) \right] (H_{B_n A}/\Delta E_{B_n A}) \quad (4.50)$$

where H_{DB_1} , $H_{B_i B_{i+1}}$ and $H_{B_n A}$ are respectively the matrix elements for the couplings between D and the first bridge unit B_1 , the i th and $(i+1)$ th bridge units, and the terminal bridge unit B_n and A, and ΔE_{DB_1} , $\Delta E_{DB_{i+1}}$ and $\Delta E_{B_n A}$ are the energy differences between D and B_1 , D and B_{i+1} , and B_n and A. An analogous expression could be written for HT via the bridge HOMOs. Equation 4.50 shows that T_{DA} (and hence k_{ET}) is greater when the energy gaps are smaller, which is why π -conjugated bridges permit faster charge transfer than do saturated bridges of the same length with higher-lying σ orbitals.

The favoured mechanism (hole or electron transfer) depends on which pathway involves the lower energy bridge orbitals: where the frontier orbitals of D and A lie closer in energy to the bridge LUMOs than to the bridge HOMOs, electron transfer from D to A via the bridge LUMOs and intermediates of the type $D^+B_i^-A$ will be dominant, but where the D and A orbitals lie closer to the bridge HOMOs, the dominant reaction channel will be hole transfer from A to D via these HOMOs and intermediates of the type $DB_i^+A^-$. A suitably chosen DBA molecule can act as a rectifying junction, with the conductance varying with the sign of the applied voltage (Metzger *et al.*, 2003).

Each factor in eq. 4.50 is much less than unity in the weak-coupling limit, so T_{DA} is decreased by each additional bridge unit, though not necessarily uniformly. Since each additional bridge unit introduces an additional overlap between wavefunctions in their exponentially falling tail regions, T_{DA} is predicted to fall off roughly, though not necessarily exactly, exponentially with increasing numbers of bridge units, and hence with D–A distance according to (*cf.* eq. 4.43)

$$T_{DA} \approx T_{DA}^0 \exp[-(\beta/2)(r_{DA} - r_{DA}^0)] \quad (4.51)$$

The early superexchange model of McConnell (1961) is a simplified version of Fig. 4.17. In this model, the frontier orbitals of D and A are assumed to have the same energy, and the n bridge units are taken to be identical. The energy offset between the D or A frontier orbitals and the bridge orbitals is designated Δ , the DB and BA couplings by the ‘hopping integral’ T , and each nearest-neighbour BB coupling by the hopping integral t . For this model in the weak interaction limit ($|T/\Delta|$, $|t/\Delta| \ll 1$), McConnell (1961) found T_{DA} as

$$T_{\text{DA}} = -(T^2/\Delta)(-t/\Delta)^{n-1} \quad (4.52)$$

This equation, which is a particular case of eq. 4.50, has several interesting implications. It predicts a strictly exponential fall-off of T_{DA} (and hence k_{ET}) with n (and hence r_{DA}). Noting from eq. 4.52 that $T_n/T_{n-1} = |t/\Delta|$, where T_n and T_{n-1} are the values of T_{DA} for supermolecules with n and $(n-1)$ bridge units respectively, and from eq. 4.43 that $T_n/T_{n-1} = \exp(-\beta\Delta r/2)$, where Δr is the width of one bridge unit, the McConnell attenuation coefficient β is found as

$$\beta = (2/\Delta r) \ln |t/\Delta| \quad (4.53)$$

Thus β is predicted to be independent of the terminal DB and BA couplings, but highly sensitive to the bridge orbital energies and couplings. Equation 4.52 also indicates that T_{DA} may show sign alternation when n changes by one, leading to the possibility of interference between ET (or HT) pathways of different length in multipath systems.

4.6.2 Evaluation of the transfer integral T_{DA}

Evaluating T_{DA} for complex and realistic DBA systems has been the goal of much theoretical work. A generic DBA system, shown in Fig. 4.18, has a multiply connective bridge incorporating many possible reaction channels, which may include non-nearest neighbour pathways, ‘back tracking’ and simultaneous movement of holes and electrons. To calculate T_{DA} , the chemical identities of D, B and A must be specified and a reasonable (though always non-unique) choice of the basis set of participating orbitals made. Taking all significant coulomb, exchange and overlap interactions into account, T_{DA} is then calculated for this basis set by *ab initio* or semiempirical methods.

The results of such computations, whilst in part particular to the system under study, allow some generalisations. There is no unique pathway for superexchange, although the lowest energy route in a well-designed D–B–A supermolecule will be overwhelmingly favoured. More generally, reaction occurs by a number of parallel pathways with a range of values of m , the number of virtual hops. Since each hop generally involves electronic attenuation, ‘as-the-crow-flies’ pathways of smaller m are however preferred, and T_{DA} is therefore much more sensitive to the nature of the material lying along the D–A axis than to the surrounding medium. Continuous covalent linkage along this axis is not necessary for through-bond superexchange; interaction between nonbonded orbitals suffices, particularly where a strong interaction is provided by, for example, hydrogen bonds. Reaction may involve more than one moving charge; mechanisms in which several electrons and holes move cooperatively are possible.

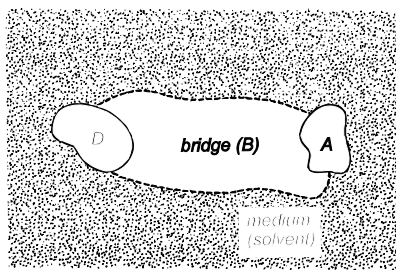


Figure 4.18 Generic model of a bridge-mediated ET system. From Newton *et al.* (1999).

If the tight-binding assumption is relaxed and non-nearest-neighbour interactions are permitted, this introduces the possibility of non-nearest-neighbour pathways for ET. Where these decrease m and increase T_{DA} , they can become the dominant route. Alternatively, non-nearest-neighbour interactions can decrease T_{DA} by destructive interference between different propagating wavefunctions, or between one propagating wavefunction and its ‘reflection’ at a bridge end. When D and A are themselves large (*e.g.* co-factors in ET proteins), superexchange can originate from various parts of the surfaces of D and A, increasing the number of pathways and the possibilities of interference still further.

T_{DA} is also sensitive to conformational changes of the DBA ensemble, especially to the orientations of D and A relative to the bridge. When the frontier orbitals of D and A are in-plane with the bridge, superexchange involves σ -orbitals of the bridge. Where they are perpendicular to the bridge, superexchange involves bridge π -orbitals (where there are any), and reaction is generally facilitated.

The effect of solvent can be investigated by adding discrete solvent molecules into the DBA ensemble (as well as a peripheral dielectric continuum). Computational results indicate that, where a covalent link connects D and A and fills the space between them, through-space and peripheral routes involving solvent molecules are unimportant. However, where solvent rather than a covalently linked bridge fills the space between D and A, the ‘as-the-crow-flies’ pathway it provides will dominate D–A coupling and the ET reaction channel.

As the above brief discussion indicates, superexchange computations have provided powerful insights into how ET occurs in a diverse range of systems. The importance of this as far as photoconversion is concerned is that rational design of PET systems—like rational design of drugs—is becoming increasingly possible by computer-based studies.

4.6.3 Distance dependence of superexchange ET rates

Both the coupling element H_{RP} (eq. 4.43) and the transfer integral T_{DA} (eq. 4.51) fall off essentially exponentially with the distance between D and A. Substituting either of these equations into eq. 4.43 gives

$$k_{\text{ET}} = \frac{2\pi}{\hbar} H_{\text{RP}}^2 (4\pi\lambda kT)^{-1/2} \exp[-\beta(r_{\text{DA}} - r_{\text{DA}}^0)] \exp\left[-\frac{(\lambda + \Delta G^0)^2}{4\lambda kT}\right] \quad (4.54)$$

for nonadiabatic transfer. Neglecting the distance dependence of λ (although this can be significant in polar media at short r_{DA}), k_{ET} is predicted to fall off exponentially with r_{DA} with attenuation coefficient β . This has been confirmed by a large number of studies on D–A and D–B–A supermolecules and assemblies in which r_{DA} is systematically varied.

The coefficient β depends on the nature of the bridge. Highly π -conjugated unsaturated bridges are among the best ‘conductors’, with β values in the range 0.5–0.9 Å^{−1}. Saturated bridges, which are typically composed of higher-lying σ -orbitals, usually have $\beta > 1$ Å^{−1}. For unlinked D and A in glassy media β is ~ 1.2 Å^{−1}. For ET proteins β is typically 1.4 Å^{−1}, reflecting the packing density of protein atoms between the redox centres (Page *et al.*, 1999). All these β values are much lower than through-space values, confirming that ET is facilitated by a bridge: the through-space value of β given by the Gamow (WKB) model, $\beta = 2(2m_e\Delta)^{1/2}/\hbar$, where m_e is the effective mass of the tunnelling electron and Δ is the (rectangular) barrier height, is ~ 2.3 Å^{−1} for $\Delta = 5$ eV.

Exponential fall-off of k_{ET} with r_{DA} is to be expected only over a limited range of distances. As r_{DA} becomes very short (with only one or two bridge units between D and A, or close contact between them), the D–A coupling is likely to become so strong that the reaction becomes adiabatic. The rate equation then takes the form (*cf.* eq. 4.29)

$$k_{\text{ET}} = \nu_n \exp\left[-\frac{(\lambda + \Delta G^0)^2}{4\lambda kT}\right] \quad (4.55)$$

where ν_n may be determined by a particular vibrational mode of the system (*e.g.* the Fe–CN stretching frequency in the $\text{Fe}(\text{CN})_6^{2-/3-}$ exchange reaction) or by solvent dynamics. Beyond some critical value of r_{DA} , on the other hand, the normal exponential fall-off with distance of the rate of coherent intramolecular ET means that superexchange will become excessively slow. A number of things may happen at this point. If the reaction is photoinduced, then decay of the excited state D* or A* *in situ* will prevent electron transfer altogether. If the D–A system is embedded in a medium of non-zero conductivity, ‘through-bath’ intramolecular channels and/or intermolecular conductance channels may switch on. Variable-range hopping is also possible if hops to sites that are

farther away in space but closer in energy exist. An important example of this in nature is the DNA double helix, which is effectively a one-dimensional molecular wire along which holes can hop, mainly from one guanine residue to the next, in an important mechanism in radiation damage and repair (Giese, 2002, 2004; Renger and Marcus, 2003). Finally, if the bridge in a D-B-A supermolecule is sufficiently coupled to D and/or A, hopping conduction (Fig. 4.16b) will take over from superexchange (Fig. 4.16a); we explore this in the next section.

4.6.4 Hopping conduction

In a D-B-A supermolecule with a short bridge ($r_{\text{DA}} = 5-10 \text{ \AA}$), superexchange is almost always the dominant mechanism of electron transfer. As the bridge length increases, the hopping conduction mechanism will start to operate in parallel with, and quickly take over from, superexchange.⁷ When hopping between bridge sites is the conduction mechanism, the D-to-A electron-transfer rate falls off linearly with distance, and the molecule becomes a linear (ohmic) resistor rather than an exponential one (Davis *et al.*, 1997). Ohmic behaviour is also to be expected of a macroscopic ensemble of molecules, even if each is individually an ‘exponential resistor’, because electrons will transfer from one molecule to the next by hopping at a rate determined by a (linear) drift field and scattering.

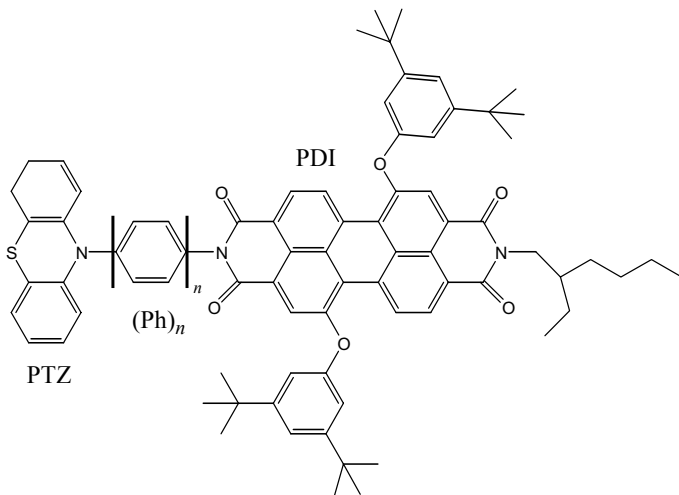
The value of r_{DA} at which the changeover from superexchange to hopping conduction occurs in a D-B-A supermolecule depends on a number of factors, notably the coupling of the bridge units with D and/or A and with each other and the temperature. Superexchange is favoured relative to the hopping mechanism by low bridge populations, and therefore by a low temperature and a high energy gap Δ ($> 0.5 \text{ eV}$) between the frontier orbitals of D or A and those of the bridge. Higher temperatures favour the changeover from superexchange to hopping because thermal activation of the first electron or hole hop is facilitated, and also because charge becomes increasingly localised in the bridge by electron-phonon interaction, and finally the formation of lattice polarons. A similar changeover from coherent band-like transport to hopping conduction is seen in bulk organic semiconductors (Schön *et al.*, 2001).

Another factor favouring the switch from superexchange to hopping conduction is the degree of delocalisation in the bridge. In D-B_n-A supermolecules with n unsaturated bridging units, the bridge states may be partly or fully delocalised. If the bridge is fully

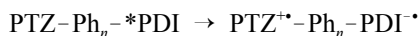
⁷ Petrov *et al.* (2001) have provided a unified theoretical description of the superexchange and hopping mechanisms.

conjugated, the bridge state will be a single delocalised state. In this case, the conjugation length will increase as extra units are added to the bridge, and the injection energy Δ will decrease, so the changeover from superexchange to hopping is facilitated. The rate of electron transfer may then become essentially independent of the number of bridging units, *i.e.* the distance between D and A. This is the behaviour sought in a molecular wire.

Figure 4.19 shows what is postulated to be a switch from superexchange to charge hopping through a single delocalised bridge state in the elegant PTZ-Ph_n-PDI supermolecules of Wasielewski and co-workers (Weiss *et al.*, 2004), shown below.

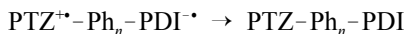


Following photoexcitation of PDI, the rate constants k_{CS} for the charge-separation step



show typical superexchange behaviour, falling exponentially with distance with decay coefficient $\beta = 0.46 \text{ \AA}^{-1}$ up to $n = 4$, but the rate constant for $n = 5$ is higher (Fig. 4.19a).

The rate constants k_{CR} for the charge-recombination process



fall exponentially for $n = 1-3$ and with the higher $\beta = 0.67 \text{ \AA}^{-1}$, but increase for $n = 4-5$ (Fig. 4.19b). The slight increase in k_{CR} for $n = 4$ and 5 may be due to the combination of the increasing electronic interaction between $\text{PTZ}^{+\bullet}\text{-Ph}_n\text{-PDI}^{\bullet-}$ and $\text{PTZ-Ph}_n^{+\bullet}\text{-PDI}^{\bullet-}$ as the energy gap between them becomes smaller and the decreasing internal reorganisation energy for putting a charge on a longer bridge (Weiss *et al.*, 2004).

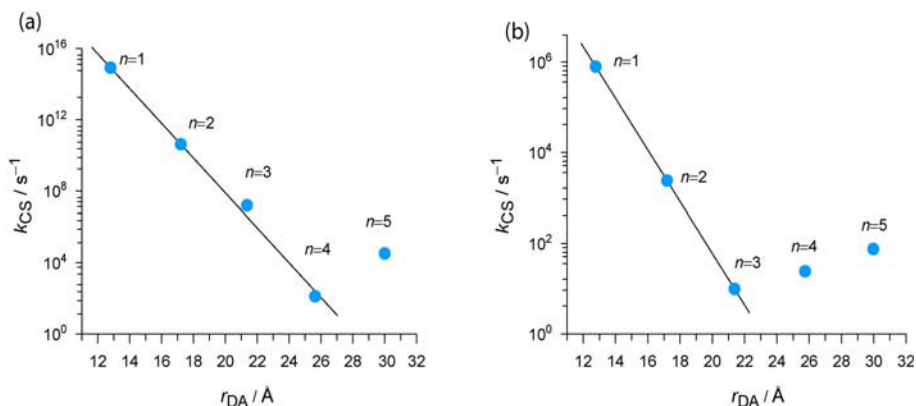


Figure 4.19 Logarithmic plots of (a) the charge-separation rate constant k_{CS} and (b) the charge-recombination rate constant k_{CR} vs. the donor-acceptor distance r_{DA} . Adapted from Weiss *et al.* (2004).

4.7 Electrochemical electron transfer

Electron transfer at an electrode (which we write $\text{Ox} + e^- \rightleftharpoons \text{Rd}$) has some similarities to homogeneous electron transfer, but also obvious differences. For a start, the ET reaction occurs across an interface between two very different phases, the solution (which is an ionic charge carrier) and the electrode (which is an electronic charge carrier). The interface is polarisable, which means that the free energy of the ET reaction can be changed by changing the electrode potential. On the solution side, the reactant (say, Ox) may be in homogeneous solution, in which case it must diffuse very close to the electrode before ET can occur, or it may already be held at the electrode by covalent linkage or adsorption. Once Ox is within reacting distance of the electrode, events on the solution side proceed much as they do in homogeneous ET, except that there is only one redox couple involved rather than two as in the case of homogeneous reaction between D and A. Thus Ox and the solvent around it must be activated to the transition-state configuration at which isoenergetic ET can occur within a fixed nuclear framework in accordance with the Franck–Condon principle. The product (Rd) is formed in this configuration and relaxes to its equilibrium configuration thereafter. Thermal fluctuations spread the energies of the Rd and Ox molecular ensembles over two gaussian distributions, which constitute the sets of occupied and unoccupied electronic states in solution respectively.

On the electrode side, in the case of a metal, there is a continuum of allowed electronic states in the conduction band that is essentially filled to the Fermi level. In the case of a semiconductor, there are two bands of allowed states, the valence and conduction bands, separated by a forbidden gap. The Fermi level normally lies within the forbidden gap. Whether the electrode is metallic or semiconducting (or indeed insulating), the addition or removal of an electron does not require any nuclear reorganisation within the electrode (except in the rare case that the electrode material is deformable so that polarons form). However, electronic polarisation of the electrode by a charged reactant or product may produce image charges in the electrode. Also the movement of an electron across the solution/electrode interface, or the movement of electronic charge within a porous electrode may require the coupled movement of charge-compensating ions in solution, slowing the overall rate of charge transfer.

ET reactions of many outer-sphere complexes at electrodes appear to be at or near the adiabatic limit (Schmickler, 1986), and to these the classical Marcus equation can be applied in the modified form

$$k_{\text{ET}}^{\text{s}} = Z_{\text{s}} \exp(-\Delta G_{\text{s}}^{\ddagger}/kT) \quad (4.56)$$

where Z_{s} ($\sim 10^4 \text{ cm s}^{-1}$) is the collision rate of a molecular species in solution with a planar surface. Where the species to be oxidised or reduced is further distant from the electrode surface, the reaction becomes nonadiabatic. In this case the high-temperature limit semiclassical Marcus equation for homogeneous ET (eq. 4.47) is usually applied, the coupling matrix element H_{RP} being calculated quantum mechanically. Feldberg and Sutin (2006) have developed a unified treatment of the distance dependence of electron transfer at an electrode through the adiabatic and nonadiabatic regimes.

Three main changes need to be made to any of the ‘homogeneous’ equations to make them appropriate for heterogeneous, *i.e.* electrochemical, electron transfer or photo-induced electron transfer (Chidsey, 1991; Marcus, 1996; Royea *et al.*, 1997). First, because the reaction involves movement of an electron across a charged interface, the potential drop across which changes with the electrode potential U , the free energy of reaction is a function of U . For the reduction (cathodic) reaction $\text{Ox} + \text{e}^- \rightarrow \text{Rd}$ we may write

$$\Delta G_{\text{c}}(U) = q(U - U^{\circ'}) \quad (4.57)$$

where $U^{\circ'}$ is the formal reduction potential of the Ox,Rd couple, *i.e.* the value of U when $c_{\text{Ox}} = c_{\text{Rd}}$. The free energy change for the oxidation (anodic) reaction $\text{Rd} \rightarrow \text{Ox} + \text{e}^-$ is simply the reverse of this, *i.e.*

$$\Delta G_{\text{a}}(U) = -q(U - U^{\circ'}) \quad (4.58)$$

These potential-dependent terms should replace ΔG° in eq. 4.47. The expression for the reorganisation energy λ also needs modification, because only one redox couple is involved in electrochemical ET and the dielectric properties of the electrode and solution are different. As with homogeneous reactions, λ is calculated as the sum of an inner and an outer contribution. The inner reorganisation energy λ_{in} arises from any structural difference between Ox and Rd, and may be calculated as⁸

$$\lambda_{\text{in}} = \sum_j \frac{f_j^{\text{Ox}} f_j^{\text{Rd}}}{(f_j^{\text{Ox}})^{1/2} + (f_j^{\text{Rd}})^{1/2}} (\Delta x_j^\circ)^2 \quad (4.59)$$

where f_j^{Ox} and f_j^{Rd} are the force constants of the j th normal mode, and Δx_j° the difference in the equilibrium values of the j th coordinate, in Ox and Rd. The inner reorganisation energy for the electrode reaction $\text{Ox} + e^- \rightleftharpoons \text{Rd}$ is roughly half that for the homogeneous self-exchange $\text{Ox} + \text{Rd}$ reaction, and is usually small.

Expressions for the outer reorganisation energy for electrochemical ET have been derived for a number of model systems. Liu and Newton (1994) give expressions for several two-zone and three-zone models. For the simplest case, a two-zone model comprising a planar infinite metal electrode contacting a solution phase containing point-charge ions, λ_{out} is given by (Marcus, 1965a)

$$\lambda_{\text{out}} = \frac{(\Delta q)^2}{4\pi\epsilon_0} \left[\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_{\text{s}}} \right] \left[\frac{1}{2r_{\text{Ox}}} - \frac{\gamma}{2d} \right] \quad (4.60)$$

where $\pm\Delta q$ is the difference between the charges on Ox and Rd (almost always ± 1 electronic charge), ϵ_{op} and ϵ_{s} are the optical and static dielectric constants of the solution, r_{Ox} is the radius of the reacting moiety (Ox or Rd), and d is the distance between it and the electrode surface. The $\gamma/2d$ term derives from interaction of $\pm\Delta q$ with its image charge in the electrode. If the electrode is a perfect conductor (a metal), an image charge forms and $\gamma = 1$; if the electrode is a poor conductor (a semiconductor) an image charge cannot form and $\gamma \rightarrow 0$. Where an image charge forms, it partly neutralises the field of the reacting ion and reduces λ_{out} , possibly by significant amounts of up to a few tenths of an eV. The screening effect of other ions in solution may, however, prevent image charge formation even at a metal electrode.

⁸ The square-root terms in eq. 4.59 come from the way that the Ox, Rd force constants are symmetrised (Brunschwig and Sutin, 1999).

A further important modification of eq. 4.47 is needed, to take account of the different band structures and carrier densities of metal and semiconductor electrodes. These behave rather differently, and we shall consider them in turn.

4.7.1 Metal electrodes

The conduction band of a metal possesses a continuum of allowed electronic states, whose effective density-of-states ρ_m (*i.e.* the number of states per atom per unit energy interval available to the redox species) may be taken to be independent of energy. The probabilities $p_e(E)$ and $p_h(E)$ that a state of energy E is occupied by an electron or hole, respectively, are given by the Fermi–Dirac function

$$p_e(E) = 1 - p_h(E) = \frac{1}{1 + \exp[(E - E_F^m)/kT]} \quad (4.61)$$

where E_F^m is the Fermi level of the metal, which is by definition the energy for which $p_e(E) = p_h(E) = 1/2$.

Electrons and holes in different states in the conduction band differ in momentum as well as energy E . For the moment, we shall assume that momentum conservation is not important during electrochemical electron transfer (ET) or hole transfer (HT) (an assumption that we shall later re-examine), but that such transfers must, as usual, occur between isoenergetic energy states within a fixed nuclear framework. That is, reduction can occur by ET from any occupied state in the electrode (roughly speaking, anywhere below the Fermi level) into an isoenergetic Ox state in solution. Similarly, oxidation can occur by HT from any vacant level in the electrode (*i.e.* anywhere above the Fermi level) into an isoenergetic Rd state in solution. On the solution side, the densities-of-states functions $D_{\text{Ox}}(E)$ and $D_{\text{Rd}}(E)$ are, as usual, taken to be two gaussian curves offset from each other by 2λ and lying symmetrically about the solution Fermi level E_F^{solu} . For aqueous solutions, E_F^{solu} can be calculated from the formal potential $U^{o'}$ of the Ox,Rd couple on the SHE scale (see Appendix 1A) as

$$E_F^{\text{solu}} = -4.44 - qU^{o'} \text{ eV} \quad (4.62)$$

since the Fermi level of the SHE on the vacuum scale is -4.44 eV (see Appendix 1A). Similar relations are known for some nonaqueous solvents.

Denoting the energy $(E - E_F^m)$ of any state in the metal with respect to the metal Fermi level as ε , the macroscopic rate constant $k_c(U)$ for reduction is obtained by summing, over all ε , the microscopic rate coefficients for ET from an occupied state of

energy ε in the electrode to a vacant (*i.e.* Ox) state of the same energy in solution. For nonadiabatic ET from a metal electrode to Ox moieties tethered a short, fixed distance r from the surface, eq. 4.47 becomes

$$k_c(U) = \frac{2\pi}{\hbar} H_m^2(r) \rho_m (4\pi\lambda kT)^{-1/2} \int_{-\infty}^{\infty} \frac{1}{1 + e^{\varepsilon/kT}} \exp \left[-\frac{\{\lambda + q(U - U^{o'}) - \varepsilon\}^2}{4\lambda kT} \right] d\varepsilon \quad (4.63)$$

where $H_m(r)$ is the coupling matrix element for the metal electrode and Ox at distance r , and λ is the reorganisation energy calculated from eqs. 4.59 and 4.60. The Fermi probability $1/(1 + e^{\varepsilon/kT})$ that a state of energy ε in the electrode is occupied swings from 1 to 0 over an energy interval of only a few kT (~ 0.1 eV at room temperature) as ε goes from negative to positive across the Fermi level, so the effective upper limit of the integral in eq. 4.63 is little greater than zero.

Similarly, the rate coefficient $k_a(U)$ for oxidation of tethered Rd is obtained by summing, over all ε , the rates for HT to Rd from unoccupied states of the same energy ε in the electrode, *i.e.*

$$k_a(U) = \frac{2\pi}{\hbar} H_m^2(r) \rho_m (4\pi\lambda kT)^{-1/2} \int_{-\infty}^{\infty} \frac{1}{1 + e^{\varepsilon/kT}} \exp \left[-\frac{\{\lambda - q(U - U^{o'}) + \varepsilon\}^2}{4\lambda kT} \right] d\varepsilon \quad (4.64)$$

where we assume that the coupling element $H_m(r)$ is the same for Rd as for Ox. The probability $p_h(E) = e^{\varepsilon/kT}/(1 + e^{\varepsilon/kT})$ that a metal state of energy ε is unoccupied falls rapidly from 1 to 0 as ε goes negative (below the Fermi level), so the effective lower limit of the integral in eq. 4.64 is little less than zero.

Figure 4.20 shows eqs. 4.63 and 4.64, plotted as the normalised rate coefficients

$$k_c^*(U) = k_c(U) / \left(\frac{2\pi}{\hbar} H_m^2(r) \rho_m \right), \quad k_a^*(U) = k_a(U) / \left(\frac{2\pi}{\hbar} H_m^2(r) \rho_m \right) \quad (4.65)$$

for three different values of the reorganisation energy λ . These vary symmetrically about $U^{o'}$, as can be seen by substituting $\varepsilon' = -\varepsilon$ in eq. 4.64. There is a 'normal Marcus region', where $k_c(U)$ and $k_a(U)$ increase with increasing driving force, at moderate overpotentials such that $|q(U - U^{o'})| < \lambda$. At low overpotentials, such that $|q(U - U^{o'})| \ll \lambda$, eqs. 4.63 and 4.64 reduce to the conventional Butler–Volmer form

$$k_c^* = k_o^* \exp[-\alpha_c q(U - U^{o'})/kT], \quad k_a^* = k_o^* \exp[+\alpha_a q(U - U^{o'})/kT] \quad (4.66)$$

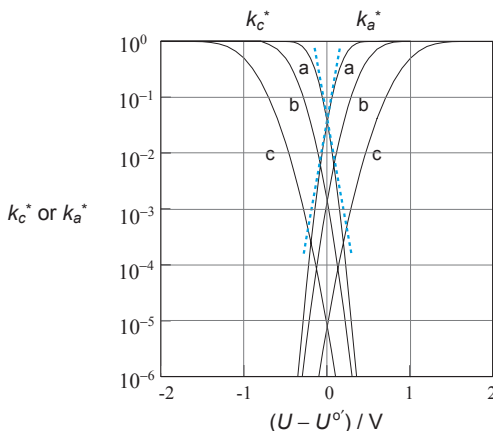


Figure 4.20 Normalised cathodic and anodic rate coefficients k_a^* and k_c^* calculated from eqs. 4.63–4.66, for $T = 298$ K and λ of (a) 0.2 eV; (b) 0.5 eV; (c) 1.0 eV. The dashed lines show the Butler–Volmer relation, eq. 4.66, for curve (a).

where α_c and α_a are the cathodic and anodic charge-transfer coefficients ($\alpha_c + \alpha_a = 1$). According to these linear free energy relations, α_c and α_a (which are the Brønsted slopes $-\text{d}[\ln k_c(U)]/\text{d}U$ and $-\text{d}[\ln k_a(U)]/\text{d}U$ shown by the dashed lines in Fig. 4.20) are constants.

At higher overpotentials,⁹ however, eqs. 4.63 and 4.64 predict that α_c and α_a will decrease towards zero, and the rate coefficients will tend to the limit $(2\pi/\hbar)|H_m|^2\rho_m$ where $|q(U - U^o')| > \lambda$. Thus the ‘inverted’ region of homogeneous ET is predicted to become an ‘abnormal’ region in metal-electrode ET, where the rate coefficients at high favourable overpotentials remain constant with increasing driving force.¹⁰

Figure 4.21 shows the reason for this in terms of the densities-of-states functions of the metal and the solution.¹¹ On the metal side at normal temperatures, the probability $p_c(E)$ that a state is occupied swings relatively sharply from 1 to 0 across the Fermi level

⁹ Strictly speaking, the term overpotential means $U - U_{\text{eq}}$, where U_{eq} is the equilibrium potential, which is not equal to the formal potential U^o' unless the concentrations of Rd and Ox are the same. Nevertheless, the term is sometimes loosely used as we do here, to denote $U - U^o'$, because it is short and expressive.

¹⁰ Conversely, the transfer coefficients are predicted to increase towards unity at unfavourable potentials. At each potential, eqs. 4.63 and 4.64 accord (as they must) with the thermodynamic relation $k_a(U)/k_c(U) = \exp[q(U - U^o')/kT]$.

¹¹ The gaussian form of the solution density-of-states functions is explained in Appendix 4A.

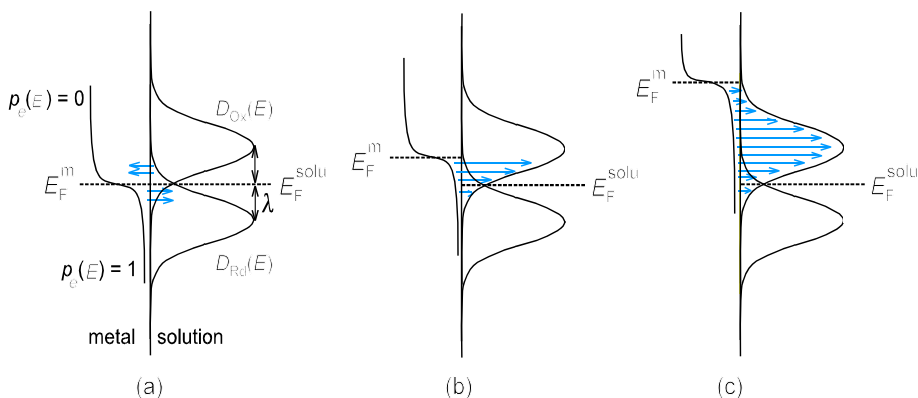


Figure 4.21 Density-of-states functions for the reaction $\text{Ox} + e^- \rightleftharpoons \text{Rd}$ at a metal electrode at (a) equilibrium; (b) a modestly negative overpotential; (c) an extreme negative overpotential. The arrows indicate the direction and magnitude of ET, as determined by the overlap of the function $p_e(E)$, which is the probability that a state in the electrode of energy u with respect to the Fermi level is occupied, with the functions $D_{\text{Rd}}(E)$ and $D_{\text{Ox}}(E)$, which are the densities of occupied and unoccupied states in solution, respectively.

compared with the bandwidth of the gaussian solution state distributions. When $U = U^{o'}$ and $c_{\text{Ox}} = c_{\text{Rd}}$ (Fig. 4.21a), the system is at equilibrium and the Fermi levels in the electrode and solution are the same. The overlap of occupied states in the metal with unoccupied states in solution is equal to that of the unoccupied states in the metal with occupied states in solution, and $k_c(U^{o'}) = k_a(U^{o'})$. If the electrode potential is taken modestly negative of $U^{o'}$ (Fig. 4.21b), raising the Fermi level in the electrode relative to that in solution by $|q(U - U^{o'})|$, the overlap between the occupied states in the electrode and the unoccupied states in solution is much improved and $k_c(U)$ is increased. (Meanwhile, the overlap between the unoccupied states in the electrode and the occupied states in solution is worse and $k_a(U)$ is decreased.) At extreme negative overpotentials (Fig. 4.21c), such that the electrode Fermi level lies essentially above the whole Ox band, the range of overlapping states tends to a potential-independent limit, so $k_c(U)$ also tends to a limit. At extreme positive overpotentials, $k_a(U)$ tends to the same limit.¹²

The coupling element $H_m(r)$ in eqs. 4.63 and 4.64 falls off exponentially in the usual manner. Consequently, electrochemical rate coefficients are predicted to fall off exponentially with increasing tether length r , and this has been verified in several studies, with β values depending on the nature of the tether and generally falling in the range $\sim 0.5\text{--}1 \text{ \AA}^{-1}$ (e.g. Finklea *et al.*, 1992; Smalley *et al.*, 1995). There is some evidence that

¹² The derivation of eqs. 4.63 and 4.64 by the overlapping density-of-states approach looks quite different from that for the rate of ET in homogeneous solution, eq. 4.47. The equivalence between the two is demonstrated in Appendix 4B.

rates tend to an upper limit as the tether becomes very short, which may indicate that the adiabaticity limit has been reached (Feldberg and Sutin, 2006).

If the redox species is not tethered to the electrode but in solution, eqs. 4.63 and 4.64 may be modified (Royea *et al.*, 1997) by replacing $|H_m(r)|^2$ by $|H_m^0|^2/\beta$, where H_m^0 is the coupling element at the distance of closest approach r_0 and β is the attenuation coefficient.¹³ If ET is adiabatic, the pre-exponential factors in eqs. 4.63 and 4.64 should be replaced by kT/h . In both cases, the nuclear terms (the integral) are unchanged, so in principle these rates should also tend to a limit at high favourable overpotentials.

The prediction of such limits rests on the integrations in eqs. 4.64 and 4.63, and these in turn rest on the assumption that momentum conservation in the electrode is not a constraint. If it were, then only electrons and holes very near the Fermi level could be involved in interfacial ET and HT, because replacement of an electron by a hole at the Fermi level does not change the electronic momentum of the solid, whereas the removal of a low-momentum electron of energy well below the Fermi level, which creates a ‘hot’ (high-momentum) hole, does. If this were a real constraint, then ET rate coefficients at metal electrodes should behave like ET rate constants for homogeneous ET, and show an inverted region past the Marcus maximum rather than tending to a limit.

Experimental evidence is to date is sparse. The range of electrode potentials over which rate coefficients may be measured is bounded by solvent decomposition, and most measurements have not spanned a sufficient range to extend beyond the normal Marcus region. Moreover, measurement of fast ET kinetics at metal electrodes is hindered by diffusion (if the redox species is in solution) and by the high capacitance of metal/solution interfaces (requiring the use of techniques that prevent the ‘RC time constant’ from dominating the dynamic response of the interface). For typical values of $\rho_m \sim 1$ state eV⁻¹, the limiting rate coefficients $(2\pi/\hbar)|H_m(r)|^2\rho_m$ are $\sim 10^{16}|H_m(r)|^2$ s⁻¹, so the coupling $H_m(r)$ must be very weak to bring them into the experimentally accessible time domain. Measurements over a wide range of electrode potentials on redox species of well-controlled and uniform distance from the electrode are required. Chidsey (1991) was among the first to conduct such studies. His rate data, shown in Fig. 4.22, clearly flatten at high favourable overpotentials, though it is not possible to decide whether they tend towards a limit or to a maximum beyond which there lies an inverted region.

If ET rate coefficients at metal electrodes tend to a limit rather than decreasing with increasingly negative $-\Delta G^\circ$, there is little opportunity for decreasing the rate of a thermodynamically favourable back ET reaction following a forward PET reaction. The implication for photoinduced electron transfer reactions at metal electrodes is that they will be ineffective as a means of net charge separation, as indeed they are. Metals are

¹³ This changes the dimensions of $k_c(U)$ and $k_a(U)$ from [time⁻¹] in eqs. 4.63 and 4.64 to [distance time⁻¹].

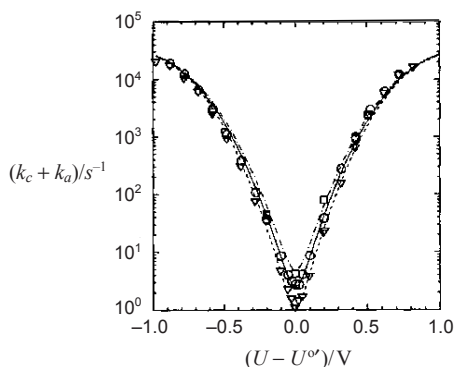


Figure 4.22 Measured rate coefficients at 25 C for a ferrocene/ferricenium derivative tethered at a fixed distance (~ 20 Å) from a gold electrode surface within an alkane thiol monolayer for four different samples (symbols), together with rate coefficients calculated from eqs. 4.63 and 4.64 with $\lambda = 0.85$ eV and the prefactor $(2\pi/\hbar)|H_m(r)|^2\rho_m = 6.73 \times 10^4 \text{ s}^{-1} \text{ eV}^{-1}$. From Chidsey (1991).

excellent quenchers of photoexcited states, because a facile forward PET reaction will be followed by an equally facile back ET reaction, as illustrated in Fig. 4.23. Still, the back reaction is slower than it would have been had Butler–Volmer kinetics held.

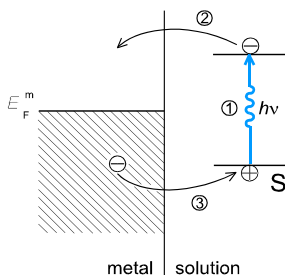


Figure 4.23 Quenching of photoexcitation at a metal electrode. On photoexcitation of a sensitizer molecule S at the metal surface (step 1), the electron readily transfers from the LUMO of S into an empty state above the Fermi level of the metal (step 2), but the hole in the HOMO is rapidly filled by back ET from an occupied state below the metal Fermi level (step 3). The order of steps 2 and 3 may be reversed but the effect is still rapidly to quench S^* .

4.7.2 Semiconductor electrodes

In a semiconductor the valence and conduction bands of allowed states are separated by a forbidden gap, usually lying in the range 1–3 eV, that contains no or few allowed states. Semiconductor electrodes are usually doped to increase their conductivity, and this affects the position of the Fermi level, E_F^{sc} . In *n*-type semiconductors, E_F^{sc} lies near the conduction band edge, and redox reactions normally involve ET with the conduction band only. In *p*-type semiconductors, E_F^{sc} lies near the valence band edge, and redox reactions normally involve HT with the valence band only. Unlike a metal, a semiconductor electrode has a space-charge layer, and when the electrode potential changes, it is the voltage drop across the space-charge layer (the band bending) that changes, not the voltage drop across the Helmholtz (compact) double layer. A consequent major difference between metal and semiconductor electrodes is that changing the potential of the latter significantly changes the concentration of electrons and holes at the electrode surface.

Figure 4.24 shows how the band bending adjusts when the potential U of an *n*-type semiconductor electrode is altered. This changes the position of the semiconductor Fermi level E_F^{sc} with respect to the solution Fermi level E_F^{solu} , at the same time adjusting the band bending across the space-charge layer, but the valence and conduction band-edge energies E_v and E_c are ‘pinned’ (constant) with respect to E_F^{solu} .¹⁴ At equilibrium (Fig. 4.24a), the Fermi level is constant across the interface, and the equilibrium band bending $q\Delta\phi_b^0$ is determined by the difference in the Fermi levels of the two uncharged phases before contact. At moderate negative overpotentials ($U - U^0$), the band-edge energies E_c and E_v are unchanged but the band bending is decreased by $q(U - U^0)$ to $q\Delta\phi_b$ (Fig. 4.24b). At the flatband potential U_{fb} (Fig. 4.24c) and beyond, there is essentially no band bending.¹⁵ Instead the Fermi level moves into the conduction band and the electrode behaves quasimetallically (that is, the surface density of allowed states is so high that the semiconductor no longer supports a space-charge layer).

¹⁴ This behaviour is observed only for reasonably defect-free semiconductors. Such a solution|semiconductor junction behaves like a metal|semiconductor Schottky junction, with the electrolyte solution playing the role of the metal. The other extreme of behaviour, a Bardeen junction in which the band bending is fixed and the band edges float with respect to the solution Fermi level, is observed in solution|semiconductor junctions with a high density of interfacial states.

¹⁵ The capacitance of the depleted interface reaches a maximum in the flatband condition. Measuring the flatband potential U_{fb} of the electrode on same scale as U^0 of the redox couple, and knowing the forbidden gap E_g and the offset (ΔE_g in Fig. 4.24) of the semiconductor Fermi level from the majority carrier band edge, enables E_c , E_v and E_F^{solu} to be placed on a common scale.

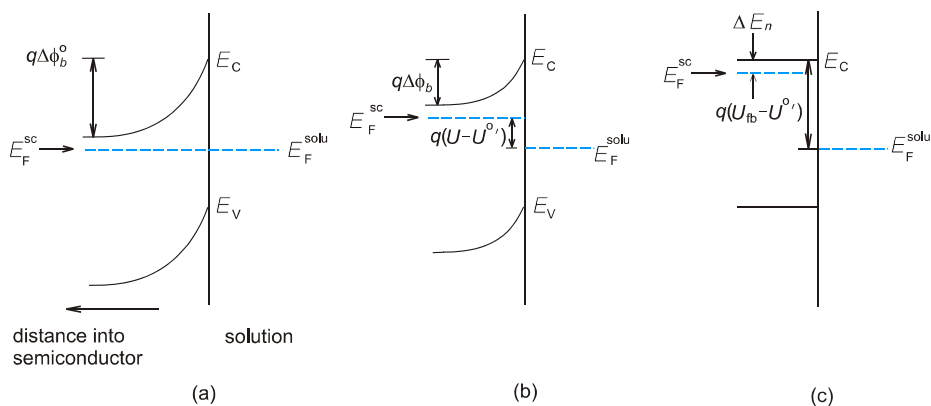


Figure 4.24 Band bending at an n -type semiconductor electrode at (a) equilibrium; (b) a negative overpotential ($U - U^0'$); (c) the flatband potential U_{fb} .

Figure 4.25 shows the relevant densities-of-states functions, again for the example of an n -type electrode. On the solution side, the density-of-states functions $D_{Ox}(E)$ and $D_{Rd}(E)$ of the Rd, Ox couple have the usual gaussian form (and we again assume these to be independent of electrode potential). On the semiconductor side, the density $D_e(E)$ of states in the conduction band increases parabolically from the band-edge energy E_c . The occupancy function $p_e(E)$ has the same Fermi–Dirac form as for a metal electrode but only its tail lies in the conduction band, where the Boltzmann approximation usually suffices.

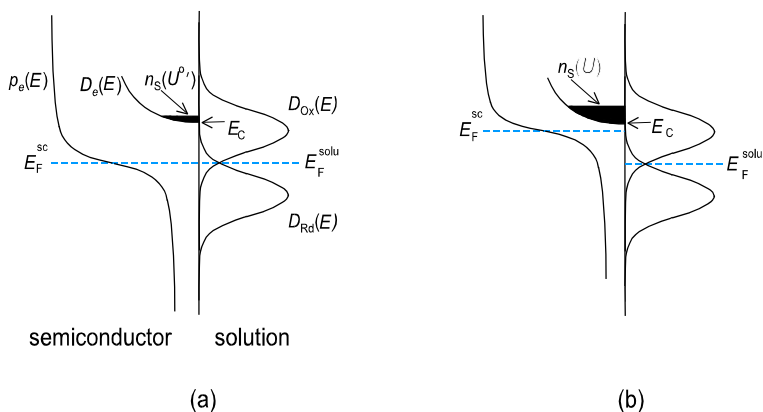


Figure 4.25 Densities-of-states functions for the solution and an n -type semiconductor electrode at (a) equilibrium and (b) a negative overpotential.

As the electrode potential is changed, the concentration of conduction-band electrons at the electrode surface changes but, because of the rapid increase in $D_e(E)$ above the band edge, their energy spread remains narrowly confined to the levels just above the band-edge energy E_c . The effective driving force for electron transfer is therefore the potential-independent quantity $(E_F^{\text{solu}} - E_c)$. For the rate $r_c(U)$ of reduction of a dissolved species Ox at an n -type semiconductor electrode, eq. 4.63 should therefore be modified to (Royea *et al.*, 1997)

$$r_c(U) = \frac{2\pi}{\hbar} H_{n-sc}^2(\bar{r})(4\pi\lambda kT)^{-1/2} c_{\text{Ox}} \exp\left[-\frac{\{\lambda + (E_F^{\text{solu}} - E_c)\}^2}{4\lambda kT}\right] \int_{E_c}^{\infty} p_e(E) D_e(E) dE \quad (4.67)$$

where $H_{n-sc}^2(\bar{r})$ is the average value of the coupling constant between the semiconductor and dissolved Ox. Provided that $p_e(E)$ can be approximated as a Boltzmann function, the integral in eq. 4.67 is the concentration $n_s(U)$ of conduction-band electrons at the electrode surface, which varies exponentially with U according to

$$n_s(U) = n_s(U^{o'}) \exp[-q(U - U^{o'})/kT]$$

The rate $r_c(U)$ of reduction of Ox can also be written

$$r_c(U) = k_{sc} n_s(U) c_{\text{Ox}}$$

and, comparing this with eq. 4.67, we see that the rate constant k_{sc} ($\text{cm}^4 \text{s}^{-1}$) for ET from an n -type semiconductor electrode is given by

$$k_{sc} = \frac{2\pi}{\hbar} H_{n-sc}^2(\bar{r})(4\pi\lambda kT)^{-1/2} \exp\left[-\frac{\{\lambda + (E_F^{\text{solu}} - E_c)\}^2}{4\lambda kT}\right] \quad (4.68)$$

The analogous expression for HT from a p -type semiconductor electrode is

$$k_{sc} = \frac{2\pi}{\hbar} H_{p-sc}^2(\bar{r})(4\pi\lambda kT)^{-1/2} \exp\left[-\frac{\{\lambda + (E_v - E_F^{\text{solu}})\}^2}{4\lambda kT}\right] \quad (4.69)$$

In contrast to the situation for a metal electrode, the rate *constant* for ET or HT at a doped semiconductor electrode is therefore independent of U . The *rate* (current) increases exponentially with overpotential because the concentration of charge carriers at the electrode surface does. In the absence of current-limiting slow steps such as diffusion, the current at a semiconductor electrode is therefore predicted to obey Butler–Volmer kinetics (up to the limit where the Boltzmann approximation to the Fermi probability function is valid).

While k_{sc} is not affected by changing the electrode potential, it is by changing the redox potential of the couple in solution. This alters the overlap of the solution density-of-states functions with the semiconductor band edges, as shown in Fig. 4.26, again for the example of a n -type electrode. If $E_{\text{F}}^{\text{solu}}$ lies only modestly below E_{c} , as in Fig. 4.26a, the nuclear overlap term at E_{c} is quite small. Figure 4.26b shows the same electrode with a more reducing couple, such that $E_{\text{c}} - E_{\text{F}}^{\text{solu}} = \lambda$. This aligns E_{c} with the maximum of the $D_{\text{Ox}}(E)$ function and maximises k_{sc} . An even more reducing couple (Fig. 4.26c) would decrease the overlap, which should cause k_{sc} to drop. In other words, semiconductor ET is predicted to show a Marcus-type inverted region, provided that all electrons are supplied at or near the band-edge energy, rather than coming from forbidden-gap surface states over a range of energies (this would produce quasimetallic behaviour).

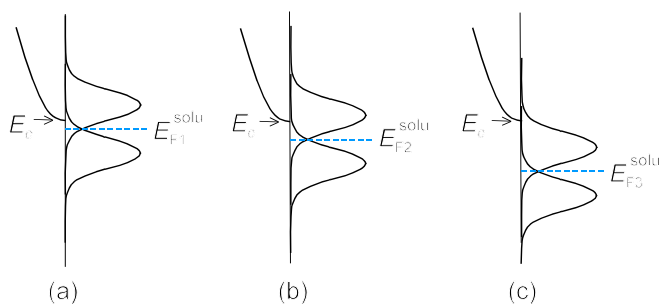


Figure 4.26 An n -type electrode with three redox couples of increasingly negative redox potential.

Both indirect and direct evidence supports this prediction. The first observation of an inverted region in semiconductor ET was made by Lu *et al.* (1993), in a study of back electron transfer from the conduction band of colloidal TiO_2 into $\text{Fe}^{\text{III}}(\text{CN})_5\text{L}^{n-}$, where L is a series of substituted pyridines. Dang and Hupp (1999) also confirmed inverted behaviour in similar experiments on back ET from SnO_2 nanoparticles into a series of $\text{Ru}^{\text{II}}\text{L}_3^{3+}$ complexes.

Indirect evidence from PET studies also points to the reality of an inverted region, in both direct and dye-sensitised charge transfer at semiconductor electrodes. That is, hole

and electron transfer is fast when the overlap of states is good, and slow when it is not, even if the transfer is thermodynamically very favourable. Another powerful factor operating in favour of productive PET in semiconductor, but not metal, electrodes is the charge-separating effect of the space-charge layer, as shown in Fig. 4.27 for the example of an *n*-type semiconductor photoelectrode. When the light is absorbed in the semiconductor (Fig. 4.27a), the photogenerated holes drift to the surface, where they oxidise the donor D, provided the overlap of the valence band edge with the gaussian manifold of D states (not shown) is reasonable. The photogenerated electrons, however, drift rapidly into the semiconductor interior and are unavailable for back ET at the semiconductor surface. Equally, when the light is absorbed by a sensitizer molecule S (Fig. 4.27b), the electron in the LUMO of S* will transfer efficiently into the semiconductor conduction band, provided its band edge is positioned below, but not too far below, the LUMO in energy. There are abundant electrons in the valence band, but they cannot transfer to the vacant state in the HOMO of S*, or its oxidation product S⁺, where the mismatch in energy levels is large.

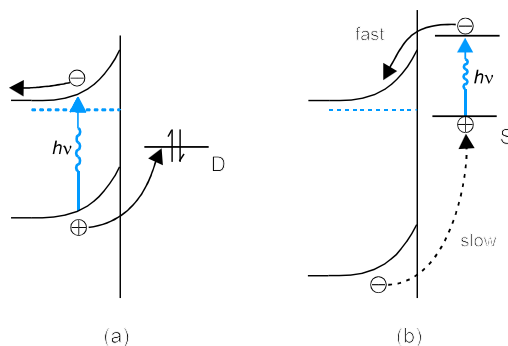


Figure 4.27 PET at an *n*-type semiconductor electrode: (a) Oxidation of an electron donor D by injection of a photogenerated hole from the valence band; (b) photosensitized electron injection from S* into the conduction band.

4.7.3 Electrochemical electron transfer through bridged assemblies

In several cases of interest in photoconversion devices, the species D or A to be oxidised or reduced at the electrode is not in close contact with the electrode surface, but deliberately separated from it by a short distance. The separator may be, for example, a thin passivating film, a molecular spacer layer or an electron-transporting bridge B in an electrode–B–A or electrode–B–D assembly such as a self-assembled monolayer (SAM).

A molecular bridge connecting an electrode to a redox moiety behaves in the same way as in a purely molecular D–B–A construct, permitting electron transfer by the superexchange mechanism up to a normal maximum of four or five bridge units. As the bridge lengthens, hopping mechanisms may operate in parallel with superexchange, and will eventually take over from it. As with electron transfer at an electrode without an intermediate bridge, the driving force for the nuclear factor in the ET rate expression is voltage-dependent, increasing with applied voltage in the normal region but decreasing in the inverted region. The electronic factors are altered by changing the separation between the electrode surface and the redox moiety or by changing the nature of the bridge. Decreasing the electronic factor for ET decreases the flux (current) at a given applied voltage in the normal region, but has a much greater effect in the inverted region (Sutin *et al.*, 2004).

4.8 Rate control by reorganisation dynamics

We have so far assumed that thermal equilibrium is maintained at every point along the reaction coordinate, that is, that the nuclear fluctuations that take the reactant complex R to the transition-state configuration $R^\ddagger$ in Fig. 4.7 are fast compared with the effective rate $\kappa_{\text{el}} \nu_n$ at which the system moves through the transition-state region. If this is so, k_{ET} will be independent of nuclear dynamics, as is usually the case, both for thermal ET and for PET reactions. However, when the transition-state crossing is very fast, the reorganisation dynamics of the solvent or an internal vibrational mode of the reactant complex can become rate-limiting.

4.8.1 Rate control by solvent dynamics

Forty years after Kramers' seminal paper on the effect of solvent dynamics on chemical reaction rates (Kramers, 1940), Zusman (1980) was the first to consider the effect of solvent dynamics on ET reactions, and later treatments have been provided by Friedman and Newton (1982), Calef and Wolynes (1983a, 1983b), Sumi and Marcus (1986), Marcus and Sumi (1986), Onuchic *et al.* (1986), Rips and Jortner (1987), Jortner and Bixon (1987) and Bixon and Jortner (1993). The response of a solvent to a change in local electric field can be characterised by a relaxation time, τ_s . For a polar solvent, τ_s is the longitudinal or 'constant charge' solvent dielectric relaxation time τ_L , given by $\tau_L = \tau_D (\epsilon_{\text{op}}/\epsilon_s)$, where τ_D is the usual 'constant field' dielectric relaxation time

(Fröhlich, 1958). For other liquids, τ_s can be estimated from dynamic simulations and usually lies in the range 1–500 ps. The rate constant is then expressed as

$$k_{\text{ET}} = k_{\text{ET}}^{\text{NA}} / (1 + g) \quad (4.70)$$

where $k_{\text{ET}}^{\text{NA}}$ is the normal nonadiabatic rate, unaffected by solvent dynamics, and g is the *solvent adiabaticity parameter*, defined as

$$g = \frac{4\pi H_{\text{RP}}^2 \tau_s}{\hbar \lambda_{\text{out}}} \quad (4.71)$$

Solvent dynamics have no influence on the ET rate when $g \ll 1$, but they start to limit the rate as g approaches 1. Substituting eqs. 4.70 and 4.71 into the high-temperature limit semiclassical equation for k_{ET} , eq. 4.47, and setting $g \gg 1$ to find the solvent-limited rate, $k_{\text{ET}}^{\text{solv}}$, we obtain

$$k_{\text{ET}}^{\text{solv}} = \frac{1}{\tau_s} \frac{\lambda_{\text{out}}}{(16\pi\lambda kT)^{1/2}} \exp \left[-\frac{(\lambda + \Delta G^0)^2}{4\lambda kT} \right] \quad (4.72)$$

The factor $\lambda_{\text{out}}/(16\pi\lambda kT)^{1/2}$ is of the order of 1, so the upper limit for the ET rate, which should be observed when $\lambda = -\Delta G^0$ and the process becomes activationless, is predicted to be $\sim 1/\tau_s$. This prediction, sensible as it seems, appears to be wrong. Femto-second lasers permit the real-time investigation of the nuclear motions accompanying ET, and it is evident from such studies that a number of ultrafast ET processes falling in the activationless or inverted regions occur on a time scale of ~ 100 –500 fs that exceeds τ_s values by factors of 50 or 100 in normal solvents, and by an even greater margin in highly viscous solvents. The extension of the theory to include the effect of specific high-frequency solvent modes fails to remove the discrepancy, and it appears that the influence of solvent dynamics on ultrafast ET is small, even in the normal region and at the Marcus maximum (Bixon and Jortner, 1993). In the inverted region, equations such as eq. 4.72 are inapplicable because of the extensive nuclear tunnelling that accompanies ET, and the effect of solvent dynamics is small.

Thus it appears that even very fast ET rates are not significantly restrained by solvent dynamics. This is an important finding as far as photoconversion is concerned since it indicates that ET (and PET) can be very fast even in viscous or rigid media.

4.9 Optimisation of photoinduced electron transfer in photoconversion

As this chapter should have demonstrated, a detailed understanding of the mechanism of ET reactions has now been achieved by the efforts of many theoreticians and experimentalists, and we shall conclude it by reflecting on the lessons for photoconversion devices based on photoinduced electron transfer reactions.

High efficiency in a PET system requires a large rate for appropriate electron transfers relative to the rate for inappropriate transfers or unproductive decay of the excited state. The ‘Marcus maximum’ and the inverted region are highly significant in this context because they provide a way of maximising the rate of the forward PET step and reducing the rate of the highly exergonic primary back ET step (both in homogeneous media and at semiconductor electrodes). Figure 4.28 illustrates the concept. By ‘tuning’ D or A and/or the surrounding medium so that $\lambda = -\Delta G^\circ$ for the forward PET step $(D, A)^* \rightarrow (D^+, A^-)$, this process becomes activationless and therefore very fast (always provided D and A are sufficiently close to each other and adequately coupled). Preferably $-\Delta G^\circ$ for the PET step should be quite low (say, ≤ 0.3 eV) because this minimises the energy loss associated with this step. To achieve the condition $\lambda = -\Delta G^\circ$, both λ_{out} and λ_{in} must also be low. For a low λ_{out} , the medium should have low polarity, and for a low λ_{in} , the excited and charge-separated states should have closely similar geometries.

The unwanted back ET reaction $(D^+, A^-) \rightarrow (D, A)$ should fall in the strongly inverted region, as shown in Fig. 4.28 and therefore be much slower than the PET step, although it is highly exergonic. Activated nuclear tunnelling, which might undermine the drop-off of ET rates in the inverted region, can be slowed by keeping the temperature low (the forward PET rate, if it is at the Marcus maximum, will be temperature-insensitive).

The powerful control exerted by the exponential dependence of ET rates on r_{DA} must also be respected and harnessed. For efficient PET, r_{DA} must be sufficiently small that electron transfer occurs well within the lifetime of the excited chromophore. For PET to occur on a picosecond time scale, edge-to-edge D–A distances must be no more than a few Ångströms. Flexibility in the charge-separated state, and the consequent formation of configurations of low r_{DA} that facilitate back ET, should also be avoided. A further powerful method of avoiding back ET is to use secondary electron acceptors and donors positioned energetically and spatially so as to draw off the charge from the primary charge-separated states before the back reaction can occur.

Natural photosynthesis, as we have already noted, seems to observe these tenets. The λ value of reaction centre protein is ≤ 0.5 eV, which is in the ballpark of the $-\Delta G^\circ$ values for the primary light-induced charge separation across a membrane, but much smaller than $-\Delta G^\circ$ values for the highly exergonic unwanted back ET step. Also the reaction centre cofactors are so positioned as to provide molecular ET stepping stones for the

electron to move across the membrane in a time short compared with the rates of excitation decay of the special pair and possible back ET steps. The main challenge now facing artificial photosynthesis is probably not the design of chromophores and supermolecules capable of efficient primary PET, but rather the creation of sufficiently sophisticated architectures to ensure efficient secondary ET, leading to storable products.

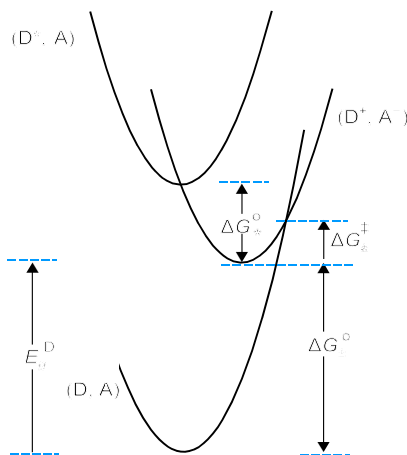


Figure 4.28 Optimal free energy surfaces for fast activationless PET from D^* to A , and slow activated ET for the back reaction of D^+ and A^- to the ground state. ΔG_0^0 is the free energy of reaction for the PET step and $\Delta G_{\pm}^{\ddagger}$ and $\Delta G_{\pm}^0$ are the free energies of activation and reaction for the back ET step from the charge-separated state ($\pm$) to the ground state. The (D^*, A) surface lies vertically above the (D, A) surface in the usual case that the geometries of D and D^* are very similar. The (D^+, A^-) surface is displaced sideways from these in the usual case that the charge-separation step is accompanied by some reorganisation.

APPENDIX 4A

SOLUTION DENSITY-OF-STATES FUNCTIONS

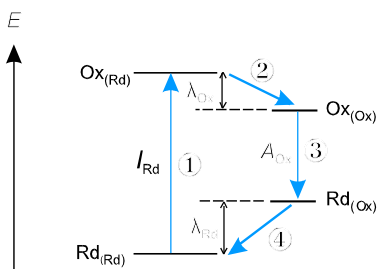


Figure 4A.1 Cycle to illustrate the reorganisation energies λ_{Ox} and λ_{Rd} of Ox and Rd in solution.

In a solid, the energy of an electronic level is usually independent of whether it is occupied or not, but this is not so for the components Rd and Ox of a Rd,Ox couple in solution. Consider the Gibbs energy cycle of Fig. 4A.1, which shows the process of transforming Rd to Ox in solution. In step 1, an electron is removed from Rd in its equilibrium configuration, denoted as $\text{Rd}_{(\text{Rd})}$. In this state, the internal structure of Rd is in its most probable configuration and the surrounding solvent is equilibrated with Rd. The ionisation is a Franck–Condon process, *i.e.* the electron is removed much faster than the nuclei of Rd or the surrounding solvent can relax, and the work done is the vertical ionisation energy I_{Rd} of Rd. The initial product of the ionisation is denoted $\text{Ox}_{(\text{Rd})}$. This is strained Ox that still has the solvation and internal configuration characteristic of Rd. In step 2, this strained configuration relaxes, forming the equilibrated structure $\text{Ox}_{(\text{Ox})}$ and releasing work λ_{Ox} . In step 3, an electron is added to $\text{Ox}_{(\text{Ox})}$ in another Franck–Condon process to form $\text{Rd}_{(\text{Ox})}$, releasing work corresponding to the electron affinity A_{Ox} of Ox.¹ The cycle is closed in step 4 as $\text{Rd}_{(\text{Ox})}$ relaxes to $\text{Rd}_{(\text{Rd})}$, releasing work λ_{Rd} . Clearly $I_{\text{Rd}} - A_{\text{Ox}} = \lambda_{\text{Ox}} + \lambda_{\text{Rd}}$. The quantities λ_{Rd} and λ_{Ox} are the reorganisation energies of Rd and Ox, *i.e.*, the work that must be done to transform the nuclear arrangement in and around equilibrated Rd to that of equilibrated Ox, and *vice versa*. These two reorganisation energies are not necessarily the same.

The mean energies of the HOMO of Rd and the LUMO of Ox are $E_{\text{Rd}}^{\circ} = -I_{\text{Rd}}$ and $E_{\text{Ox}}^{\circ} = -A_{\text{Ox}}$, respectively. In solution, internal vibrations and fluctuating solvent motions disperse the energy of a set of Ox and Rd moieties about these time-averaged means. In

¹ There is no change in nuclear configuration in steps 1 and 3, and therefore the potential energy changes I_{Rd} and A_{Ox} are also Gibbs energy changes.

classical Marcus theory, all internal and solvent distortions are taken to be classical (unquantised) and harmonic, meaning that the energy varies as the square of the displacement from the equilibrium configuration. The resulting density-of-states functions $D(E)$ are gaussian in form.

Since λ_{Rd} and λ_{Ox} are usually not known individually (nor can different values be accommodated within classical Marcus theory), their symmetrised value

$$\lambda = \lambda_{\text{Ox}}\lambda_{\text{Rd}} / (\lambda_{\text{Ox}} + \lambda_{\text{Rd}})$$

is used to describe symmetrised density-of-states functions

$$D_{\text{Ox}}(E) = (4\pi\lambda kT)^{-1/2} \exp\left[-\frac{(E_{\text{Ox,Rd}}^0 - \lambda - E)^2}{4\lambda kT}\right] \quad (4A.1)$$

$$D_{\text{Rd}}(E) = (4\pi\lambda kT)^{-1/2} \exp\left[-\frac{(E_{\text{Ox,Rd}}^0 - \lambda - E)^2}{4\lambda kT}\right] \quad (4A.2)$$

where the prefactors normalise each distribution, such that $\int_{-\infty}^{\infty} D(E)dE = 1$.

APPENDIX 4B

DERIVATION OF HIGH-TEMPERATURE LIMIT MARCUS RATE EQUATION FOR HOMOGENEOUS ELECTRON TRANSFER USING DENSITY-OF-STATES APPROACH

The high-temperature limit semiclassical Marcus expression for the rate of ET in homogeneous solution, eq. 4.47, and the expressions for the rate of ET at an electrode (eqs. 4.63 and 4.64) were derived by different approaches, which makes it hard to see that there is a link between them. Here we demonstrate this link by deriving eq. 4.47 using the overlapping density-of-states approach used to derive eqs. 4.63 and 4.64.

In the case of electrochemical ET, the relevant overlap was between the gaussian density-of-states function of the reacting species in solution and the Fermi-Dirac distribution function of the charge carriers in the electrode (Fig. 4.21). Figure 4B.1 shows the analogous density-of-states functions for a homogeneous ET reaction. The rate

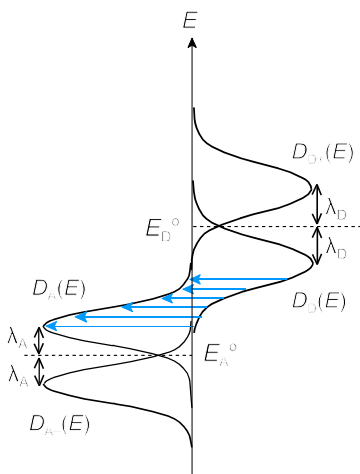


Figure 4B.1 Density-of-states functions for the reaction $D + A \rightleftharpoons D^+ + A^-$ in homogeneous solution.

constant is found by calculating the overlap between the density-of-states functions for D and A:

$$k_{\text{ET}} = \frac{2\pi}{\hbar} H_{\text{RP}}^2 \int_{-\infty}^{\infty} D_{\text{D}}(E) D_{\text{A}}(E) dE \quad (4B.1)$$

Using eqs. 4A.1 and 4A.2, eq. 4B.1 becomes

$$k_{\text{ET}} = \frac{2\pi}{\hbar} H_{\text{RP}}^2 \frac{1}{4\pi kT(\lambda_{\text{D}}\lambda_{\text{A}})^{1/2}} \int_{-\infty}^{\infty} \exp\left[-\frac{(E_{\text{D}}^0 - \lambda_{\text{D}} - E)^2}{4\lambda_{\text{D}}kT}\right] \exp\left[-\frac{(E_{\text{A}}^0 + \lambda_{\text{A}} - E)^2}{4\lambda_{\text{A}}kT}\right] dE \quad (4B.2)$$

The definite integral ($-\infty$ to $+\infty$) of a product of gaussians is

$$\int_{-\infty}^{\infty} \{\exp[-ay^2]\} \{\exp[-b(y+\Delta y)^2]\} dy = \sqrt{\frac{\pi}{a+b}} \exp\left[-\frac{\Delta y^2}{(1/a) + (1/b)}\right] \quad (4B.3)$$

It follows directly that eq. 4B.2 can be rearranged to

$$k_{\text{ET}} = \frac{2\pi}{\hbar} H_{\text{RP}}^2 \frac{1}{[4\pi kT(\lambda_{\text{D}} + \lambda_{\text{A}})]^{1/2}} \exp \left[-\frac{(E_{\text{A}}^{\circ} - E_{\text{D}}^{\circ} + \lambda_{\text{D}} + \lambda_{\text{A}})^2}{4(\lambda_{\text{D}} + \lambda_{\text{A}})kT} \right] \quad (4\text{B.4})$$

This is identical with the high-temperature limit semiclassical equation, eq. 4.47, provided that the reorganisation energy λ for the reaction can be taken as equal to $(\lambda_{\text{A}} + \lambda_{\text{D}})$. Thus this method of derivation is appropriate only for the limiting case that there is no interaction between the solvent spheres of D and A. The method presented in Section 4.5 is more general in that it allows for $\lambda \neq (\lambda_{\text{A}} + \lambda_{\text{D}})$.

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CHAPTER 5

FUNDAMENTALS IN METAL-OXIDE HETEROGENEOUS PHOTOCATALYSIS

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*The Sun offers an abundant supply of clean, renewable energy that can be harnessed
to destroy pollutants and produce chemicals.*

F. W. Wilkins and D. M. Blake, *Chem. Engr. Prog.*, June 1994.

5.1 Introduction

Metal-oxide heterogeneous photocatalysis had, if not its debut, certainly its development, with the studies of the late 1970s and 1980s (Fox and Dulay, 1993) that explored ways to photogenerate clean alternative fuels (*e.g.* H₂ from the splitting of water) with the realisation that processes carried out with organised assemblies afforded some advantages (for instance, suppression of energy-wasting back electron transfer) over homogeneous processes. In particular, semiconductor systems provided some interesting features, not least of which were stability and the possibility that the semiconductor particle surface could be modified, itself having good catalytic properties, by addition of functional or bifunctional co-catalysts (*e.g.* Pt, RuO₂ and others) to improve catalytic functions and to accentuate process dynamics. The search for solar energy conversion devices provided the impetus that ultimately led to significant development of this field.

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The field has witnessed important advances during the last two decades. Active players such as Ollis and the former Texas GRI (Gas Research Institute) group of Bard, Fox and others (USA), Pelizzetti (Italy), Serpone (Canada), Pichat (France), Grätzel (Switzerland), Matthews (Australia), and the groups of Fujishima, Anpo and Hidaka in Japan (among others) have been actively engaged in exploring illuminated semiconductor particulates aimed at production of hydrogen from water-splitting processes and/or the photooxidation of organic substrates, which were recognised early on as the sacrificial lambs (electron donors) in such energy conversion processes. An international conference, the first of its kind on 'TiO₂ photocatalysed purification of air and water', held in the early 1990s, saw no less than some 200 active participants engaged in this field (Al-Ekabi, 1992). Nearly half of the attendees came from the industrial sector, no doubt because of the seemingly facile phenomenological approach to heterogeneous photocatalysis. However, as we will see throughout this chapter, closer examination revealed significant gaps in our fundamental understanding of the events that underlie heterogeneous photocatalysis.

Consequently, studies were needed to demonstrate the general usefulness of photocatalysis and to further its development toward a viable technology that would have potential attributes in energy conversion and in resolving environmental issues. Studies were also needed to unravel and understand the events that take place at the metal-oxide particle surface and at the particle/solution or particle/gas interfaces by application of various tools, such as time-resolved spectroscopic methods (*e.g.* picosecond laser spectroscopy, electron paramagnetic resonance spectroscopy) and others. Since those early days, nearly all surface science techniques have now been brought to bear on this very important area. Our own focus was to follow the course of events from the initial interaction between UV/visible photons with the semiconductor system. Thus our interest has been to query the nature of interfacial events and the intermediates during the mineralisation of noxious organic pollutants to carbon dioxide and the removal of toxic and precious/strategic metals from wastewaters, groundwaters and industrial waste effluents.

Accordingly, many of these studies examined the primary photocatalytic events that involve (a) absorption of light, (b) formation of free carriers (electrons and holes) and/or trapped carriers (electrons as Ti³⁺ in the case of TiO₂, and holes as [•]OH radicals), and (c) reaction of preadsorbed acceptor or donor molecules with the relevant trapped carriers. This approach was reasonable when the only purpose of photocatalysis was elimination of undesirable environmental pollutants. However, when we queried how to render a process more efficient, it became evident that we needed to address more fundamental questions, namely the nature of the primary events that follow photoexcitation of the photocatalyst. In most instances, our

photocatalyst of choice has been TiO_2 (anatase titania:). Owing to the nature of light absorption by TiO_2 , the absorption onset of UV light begins around 387 nm (equivalent to a bandgap energy $E_g \sim 3.2$ eV) and increases to shorter wavelengths. Other metal oxides were also examined, many of which are dielectric insulators with very large bandgap energies, such as zirconia (ZrO_2) and scandia (Sc_2O_3). These dielectrics have provided additional useful information about the photophysical events in metal oxides, many of which tend to be masked by strong light absorption by TiO_2 .

The great interest in studies of photoinduced processes in heterogeneous systems is then not surprising. To appreciate this, we need only look around us to discover surfaces (on soil, buildings, walls, streets and elsewhere) that are interfaces between solid, liquid and gas phases. When exposed to sunlight these surfaces reflect and scatter incident solar radiation. A world of coloured surfaces can be enjoyed because of the selective absorption of sunlight by entities at such interfaces, the effect of which is to create thermodynamically open heterogeneous systems with flow of free energy of light. It is relevant to query (i) how such systems convert this free energy, (ii) what the consequences of light energy conversion in heterogeneous systems are, (iii) what parameters govern and are responsible for the photostability, photosensitivity and photoactivity of metal-oxide materials in heterogeneous systems, and not least (iv) what factors control photoinduced processes. These are but a few of the questions with which Nature has collectively challenged and engaged us in exploring photostimulated processes that take place in heterogeneous systems.

5.2 The complex science underlying metal-oxide photocatalysis

Understanding heterogeneous photocatalysis has necessitated a suitable description of (a) (photo)catalysis, (b) turnover quantities (numbers, TON; rates, TOR; frequencies, TOF), (c) quantum yields ϕ of a given process, and not least (d) the Langmuir–Hinshelwood kinetic model which has been used (though often incorrectly—see Emeline *et al.*, 2000b; Ollis, 2005) to describe process kinetics, and to deduce that the redox reactions occur at the surface of particles. It cannot be overemphasised, however, that photocatalytic events are model-independent and may simply be a manifestation of a more broadly and commonly observed saturation-type kinetics at high concentrations of one reagent in bimolecular reactions, a well-known phenomenon in chemical kinetics, even in the homogenous phase.

To start with the first question, what is photocatalysis? Or, to be more precise, what is heterogeneous photocatalysis? There is no simple answer to this question. To put it briefly, the term ‘heterogeneous photocatalysis’ has come to describe a process

whereby illumination of semiconductor particulates with UV/visible photons of energy greater than or equal to the bandgap energy of the semiconductor generates conduction-band (CB) electrons and valence-band (VB) holes which, after their separation by the electric-field gradient in the space-charge layer of the semiconductor and migration to the surface, are poised at the particle/solution interface ready to initiate redox events in competition with self-recombination.

The energy level of the bottom of the conduction band is taken as a measure of the reduction potential of photogenerated electrons; the upper level of the valence band is considered a measure of the oxidation potential of photogenerated holes. The flatband potentials, V_{fb} ,² of the conduction and valence bands, which are fixed by the nature of the material and, in the case of metal oxides, by (pH-dependent) proton exchange equilibria at the interface, determine the energy of electrons and holes at the interface. Hence, reductive processes of couples with redox potentials more positive than the V_{fb} of the conduction band can be driven by surface-trapped electrons, and oxidative processes with redox potentials more negative than the V_{fb} of the valence band can be driven by surface-trapped holes. The charge carriers (e^- and h^+) are ultimately poised at the particle surface to engage in various processes, the most important of which are photoreductions (*e.g.* of metal ions such as those of Au, Pt, Ag, Rh, Hg and Pb) and photooxidations of a large variety of organic substances (*e.g.* surfactants, pesticides and herbicides) by their complete mineralisation to carbon dioxide. Most research efforts in this area have focused on assessing the factors that underlie the temporal evolution of redox reactions taking place predominantly on metal-oxide materials (Emeline *et al.*, 1998a, 1998b, 1998c, 1999a, 1999b, 1999c, 2000a). Photoexcited semiconductor particles function as pools of electrons and holes, which can be exploited in a variety of multielectron transfer processes. The presence of a redox catalyst such as Pt or RuO_2 on the particle surface greatly improves the catalytic efficacy of the process. The smaller size particles display unusually high light absorption cross sections, fast carrier diffusion to the solid/electrolyte interface and large catalytic surfaces, and can thereby lead to highly efficient processes. Noble metal islands can be photodeposited on metal-oxide particles with remarkably high quantum efficiencies. Such metal deposits usually lead to more efficient charge separation since the particle becomes polarised subsequent to irradiation of the metal oxides, with the deposits tending to be good electron sinks. Often, however, such deposits, or so-called dopants, act as recombination centres of photoelectrons and photoholes and compromise redox efficiency.

² In a system with band-edge pinning, the flatband potentials are to the potentials at which there is no band bending.

The efficacy of semiconductor devices in photocatalysis is typically described by the quantum yield ϕ . While determining this parameter in homogeneous photochemistry presents no great difficulties, in heterogeneous media the challenges have been insurmountable to many workers for several years owing to the lack of an appropriate protocol. This was remedied by Serpone and Salinaro (1999), and appropriate experimental details were enumerated by Salinaro *et al.* (1999). Another useful parameter, the relative photonic efficiency ξ_{rel} (defined in Section 5.4.1) also provided a method by which work from many laboratories in environmental photochemistry could be calibrated when the more fundamental parameter ϕ could not be accessed because of experimental limitations (Salinaro *et al.*, 1999).

Turnover numbers and turnover rates are relatively easily measured in homogeneous (photo)catalysis; however, their determination has eluded several attempts in heterogeneous (photo)catalysis because of the required knowledge of the number of (photo)catalytically active sites on a (solid) photocatalyst. These turnovers appear to depend on how the (photo)catalytic process is described (Serpone *et al.*, 2000).

It is obvious from the above discussion that we need to examine the properties of the metal-oxide materials in some depth before we delve into the intricacies of photocatalysis which it is the main purpose of this chapter to describe.

5.2.1 Small-size semiconductor particles: optical properties

Nanosized semiconductor clusters and particles are of considerable interest in optoelectronics and energy conversion devices. Ultrasmall crystallites (clusters) composed of a few molecular units maintain their discrete HOMOs and LUMOs and the quantised energy levels within them (and the particles are often known as Q particles or quantum dots) because of the confinement of charge carriers in potential wells of small dimensions. Size quantisation in semiconductor materials causes large changes in optical properties. Accumulation of charge carriers in a small reaction volume increases the effective bandgap, and hence enhances the effective redox potentials of the photogenerated electrons and holes. Consequently, it enhances their photoredox chemistry with electron acceptors and electron donors, respectively, especially so when the particles are quantised.

Two semiconductor materials—*n*-type CdS and TiO₂—have been the focus of much attention in such photocatalytic processes as the photocleavage of water and hydrogen sulphide, and the photooxidation of alcohols, carboxylates and various other organics. The majority of photoinduced processes on these materials are examined when they are in powder form. Enquiries into photocatalytic processes centre on the

nature and identity of the primary events that immediately follow light excitation. Powders are rather opaque to irradiation, and so Rayleigh scattering is too severe for information on these primary events to be established by optical spectroscopic techniques. Therefore colloidal sols with particle sizes less than ~ 10 nm diameter have been used since they are transparent and render it possible to use optical methods to monitor events immediately after light excitation, as can be done for homogeneous systems. The success, or in some cases the lack of it, of CdS and TiO₂ in photocatalysis underlines the need for a fundamental understanding of the basic properties of semiconductor materials.

There is no doubt that TiO₂ has been the most examined semiconductor in heterogeneous photocatalysis. Serpone and Pelizzetti (1986) have reviewed work on the photophysics of CdS and TiO₂ that pre-dates 1985. A later review by Kamat (1993) summarised the remarkable progress made during the decade 1984–1993. Our studies in this area, in February–April 1983, in which picosecond pulsed-laser spectroscopic methods were employed for the first time on particulate materials, were rather revealing. As early as the autumn of 1984, we recognised the need (Serpone *et al.*, 1985a) to explore the ultrafast events that take place in this semiconductor by time-resolved spectroscopic techniques in the picosecond time domain following our earlier work on colloidal CdS sols. The photophysics of photogenerated charge carriers were elucidated using 6 nm radius TiO₂ semiconductor particles and reported by Rothenberger *et al.* (1985). The transient absorption spectrum of a TiO₂ colloidal sol (Fig. 5.1) 20 ps after excitation exhibits a rather broad band centred around 620 nm, which is nearly identical to the absorption spectrum of the electrons produced in acidic TiO₂ sols by continuous illumination in the presence of a hole scavenger. The observed spectral features in the visible region suggested that at least some of the electrons are trapped in less than 20 ps at Ti⁴⁺ sites located at the particle/water interface (reaction 5.1).



The average transit time for the electrons to reach the surface was estimated at ~ 1.8 ps. By contrast, the trapping of the valence-band holes, presumably by surface OH[−] groups or surface-chemisorbed H₂O, is a much slower process, requiring an average time of ~ 250 ns. The spectral features decayed almost entirely in the picosecond time domain without changes in the positions of the band maxima, the electron decay following second-order kinetics. Under the conditions of the experiment of Fig. 5.1, about 67 electron–hole pairs per particle were photogenerated through light activation of TiO₂, a concentration which increased with increase in the

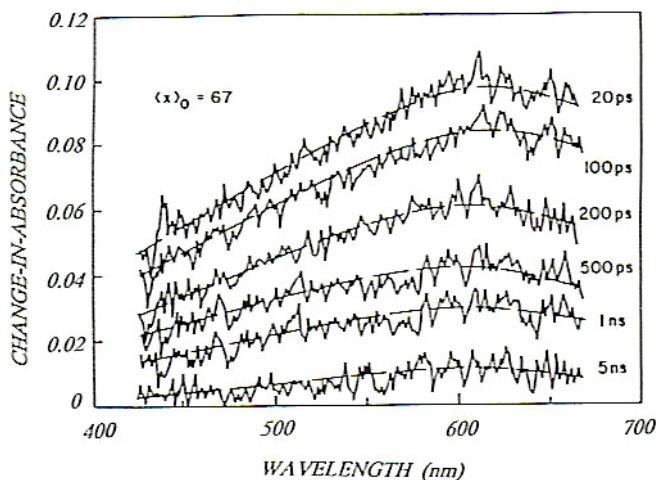


Figure 5.1 Transient absorption spectra observed at various time intervals after picosecond laser excitation of colloidal TiO_2 aqueous sols; $\langle x \rangle_0$ is the average number of electron-hole pairs present initially in one TiO_2 particle. Reprinted with permission from Rothenberger *et al.* (1985). Copyright (1985) American Chemical Society.

laser fluence up to 300 electron-hole pairs (charge carrier density $\sim 4.5 \times 10^{20} \text{ cm}^{-3}$). At these higher fluences, the spectral features remained the same, but the charge-carrier relaxation between trapped electrons and holes was faster: reaction 5.2 has a rate coefficient $k = 3.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

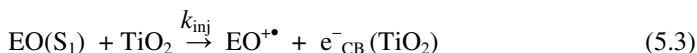


At very low occupancy of the semiconductor particles of less than one electron-hole pair per particle, such as might be produced by nanosecond laser excitation, electron-hole pair recombination became first order, with the mean lifetime of a single e^-/h^+ pair being $\sim 30 \text{ ns}$. Under such conditions, hole trapping at the particle surface and in the lattice is able to compete with charge-carrier recombination. In the trapped state, the hole is relatively unreactive toward electrons that survive in the particles for several microseconds, thus explaining the earlier findings in interfacial electron transfer between TiO_2 sols and methyl viologen, in which charge transfer occurred in the time range 10^{-6} – 10^{-3} s (Rothenberger *et al.*, 1985).

The fact that recombination of electrons with free holes is about ten times faster than hole trapping is disadvantageous if TiO_2 is to be used for light-induced water splitting. This also rationalises earlier observations that highly active surface co-catalysts (*e.g.* Pt and RuO_2) are needed on the titania particle surface to improve the

competitiveness of the surface redox chemistry. Subsequent studies by Moser (1986) and Lawless (1993) showed that the rate of electron-hole recombination could be accelerated or retarded by doping the lattice of colloidal particles with suitable transition metal ions, which can act either as electron traps or recombination centres.

The first picosecond time-resolved observations of a photosensitised charge-injection process in semiconductor particles were carried out by Moser *et al.* (1985). The rate of electron injection from the excited singlet state of the surface-adsorbed dye eosin, EO(S₁), to the conduction band of colloidal TiO₂ particles



was measured, yielding the rate constant $k_{\text{inj}} = 9.5 \times 10^8 \text{ s}^{-1}$ at 298 K and pH 3, in good agreement with the earlier finding from nanosecond laser studies of $8.5 \times 10^8 \text{ s}^{-1}$ (Moser and Grätzel, 1984). The rate of intersystem crossing from the singlet to the triplet state of eosin was $5 \times 10^8 \text{ s}^{-1}$, while the time constant for the growth of the eosin cation radical EO^{•+} was ~0.4 ns, which also denotes the lifetime of the EO(S₁) singlet state. The reorganisation energy for heterogeneous electron transfer was estimated as ~0.4 eV.

Subsequently, photoinduced interfacial electron transfer from the conduction band of colloidal TiO₂ to dimeric viologen, DV⁴⁺, an electron acceptor, was also examined by picosecond time-resolved methods (Serpone *et al.*, 1987). Electron transfer takes place in the picosecond time domain; $k_{\text{ej}} \cong 2.5 \times 10^{10} \text{ s}^{-1}$ at pH 7.8. The reaction involves consecutive one-electron transfer to give the mono-reduced DV³⁺ initially, followed by formation of DV²⁺. In acidic aqueous media (pH 3.5), transient absorption spectra showed that electron transfer does not proceed beyond the formation of the mono-reduced species.

Around the time of our first report on the picosecond spectral properties and photophysical events in titania colloids of particle diameter ~12 nm, a number of other reports concerning the photophysics of TiO₂ sols showed that particle size can have a pronounced effect on spectral properties and charge-carrier dynamics. Later reports indicated that small TiO₂ colloid particles in the size range about 1–12 nm display exciton confinement and thus size quantisation effects. However, this was later disputed by Serpone and co-workers (1995a, 1995b). Systematic studies of the dependence of the photophysical properties of TiO₂ on particle size always failed to keep pace with studies in heterogeneous photocatalysis where TiO₂ played a very significant role.

Figure 5.2 illustrates a typical spherically-shaped small TiO₂ particle, taken here as a model of small semiconductor systems, with a definition of the conduction and

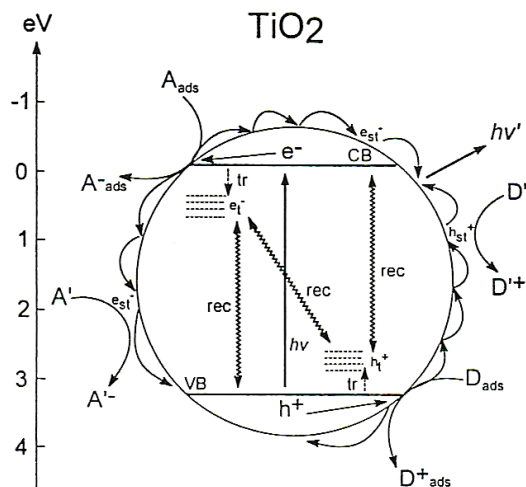


Figure 5.2 Illustration of some important photophysical events in a small semiconductor particle such as TiO_2 . The electron energy scale is referenced to CB = 0. Reprinted with permission from Serpone *et al.* (1995b). Copyright (1995) American Chemical Society.

valence bands and some (but by no means all) of the photophysical and photochemical events that might take place in the lattice and on the illuminated particle surface. After photogeneration of CB electrons and VB holes by bandgap excitation of anatase titania particles, the charge carriers can undergo a number of photophysical events. Colloidal semiconductor particulates contain a high density of lattice defect sites and surface states, the nature of which is highly dependent on the method(s) of preparation. These defects have some influence on the photophysical processes. As illustrated in Fig. 5.2, charge carriers can migrate to the surface, where they can react in competition with trapping, detrapping, and radiative and non-radiative recombination. The figure also shows that on the surface the two charge carriers can react with pre-adsorbed electron acceptors A and donors D. In the case of TiO_2 , the D donors are the surface-chemisorbed OH^- groups and chemisorbed H_2O molecules; the oxidised donors D^+ are $\cdot\text{OH}$ radicals. Species A is the ubiquitous pre-adsorbed molecular O_2 , which yields superoxide radical anion, $\text{O}_2^{\cdot-}$, as the reduced donor A^- species. We have long held the view that surface-trapped holes are nothing but the surface-bound $\cdot\text{OH}$ radical at ambient temperature, and that $\cdot\text{OH}$ radicals are the principal oxidising entities in photooxidations. The lifetime of surface-bound $\cdot\text{OH}$ is a few microseconds, long enough for an electron donor D' to be oxidised to D'^+ or to form an $\cdot\text{OH}$ adduct, $\text{D}'-\cdot\text{OH}$. Another feature depicted in Fig. 5.2 is the possibility

that charge carriers migrate along the particle surface where they are trapped and recombine in competition with redox chemistry. Such migration is reminiscent of the spillover effect involving hydrogen atoms in catalysis. The extent of migration will depend on the depth of the surface traps for electrons and holes.

For a size-quantised particle, the increase ΔE_g in bandgap energy from the bulk value varies with the particle radius, R_{part} , according to

$$\Delta E_g = \frac{h^2}{8 \mu R_{\text{part}}^2} - \frac{1.8 q^2}{\epsilon_s R_{\text{part}}} \quad (5.4)$$

where μ is the reduced effective mass of an exciton and ϵ_s is the static dielectric constant of the semiconductor, which for TiO_2 is 184. The reduced effective mass of the exciton is given by $\mu^{-1} = m_e^{-1} + m_h^{-1}$, where m_e and m_h are the effective masses of electrons and holes, respectively (Brus, 1986). For TiO_2 , Kormann *et al.* (1988) estimated μ to be $1.63m_e$, whereas Kasinski and co-workers (1989) reported a value of $2.72m_e$. Clearly, ΔE_g depends critically on the effective masses of electrons and holes; for TiO_2 m_e was taken by some to range from $5m_0$ to $13m_0$ (where m_0 is the electron rest mass), whereas others took m_e to be equivalent to $30m_0$, and m_h to $3m_0$. Exciton radii R_{exc} between $7.5 \text{ \AA}$ and $19 \text{ \AA}$ were estimated for extremely small particles of TiO_2 from the relation

$$R_{\text{exc}} = \frac{\epsilon_s a_0 m_0}{\mu} \quad (5.5)$$

where a_0 is the Bohr radius of the hydrogen atom ($0.53 \text{ \AA}$). Grätzel (1989) estimated an exciton radius of $\sim 3 \text{ \AA}$ if contributions from valence-band holes are neglected. On this basis, TiO_2 particles should display a Q-size threshold at $2R_{\text{part}} < 15\text{--}38 \text{ \AA}$ by some estimates or at $2R_{\text{part}} < 6 \text{ \AA}$ by others. Predictions of the thresholds of quantum-size effects depend critically on the magnitude of the effective mass of the electron.

A few reports in the last two decades have described exciton confinement in small TiO_2 particles. Anpo and co-workers (1987) prepared particles of titania with sizes (diameters) ranging from $55 \text{ \AA}$ to $2000 \text{ \AA}$ for rutile, and from $38 \text{ \AA}$ to $530 \text{ \AA}$ for the anatase form of TiO_2 , and noted that these crystallites display size quantisation in optical properties and in the photocatalytic hydrogenation of methylacetylene, even for such large sizes. For a $120 \text{ \AA}$ rutile particle the bandgap increased by 67 meV relative to the bulk rutile bandgap ($E_g \approx 3.03 \text{ eV}$); for anatase E_g increased by 156 meV (from the bulk E_g of $\sim 3.18 \text{ eV}$). Moreover, quantum yields of photocatalytic activity of TiO_2 appeared to increase with the magnitude of the blue shift of the effective bandgap. Kormann *et al.* (1988) indicated that small particles of TiO_2 , prepared by the arrested hydrolysis of either TiCl_4 or $\text{Ti}(i\text{-PrO})_4$, showed size

quantisation when $2R_{\text{part}} = 20\text{--}40 \text{ \AA}$. The particles exhibited a 150–170 meV blue shift of the UV absorption edge (bandgap) under anaerobic illumination, which Kormann and co-workers assigned to exciton confinement within the small TiO_2 particles due to the presence of Ti^{3+} centres (*i.e.* trapped negative charge). Others suggested that this shift from the bandgap of bulk anatase, also exhibited by $R_{\text{part}} = 25\text{--}100 \text{ \AA}$ particles, was due to a Burstein–Moss effect (Pankove, 1975). For TiO_2 particles of $2R_{\text{part}} = 10\text{--}20 \text{ \AA}$, Kavan *et al.* (1993) reported a bandgap shift of $\sim 100 \text{ meV}$, which was also attributed to a Q-size effect. These authors used low-intensity illumination to minimise the significance of the Burstein–Moss shift. Joselevich and Willner (1994) observed the onset of the absorption edge in TiO_2 (particles prepared in a water-in-oil microemulsion) to be 3.6 eV ($\lambda = 345 \text{ nm}$): the blue shift was 400 meV if the particles were anatase TiO_2 , and 600 meV if they were rutile TiO_2 . The estimated size of the particles (eq. 5.4) was $2R_{\text{part}} = 15 \text{ \AA}$ (if anatase) and $12 \text{ \AA}$ (if rutile); dilution of the colloidal sol from 0.5 g L^{-1} to 0.1 g L^{-1} had no effect on the absorption edge.

The expression for ΔE_g (eq. 5.4) has often been used to calculate the size of small semiconductor particulates for comparison with sizes measured by transmission electron microscopy. Expression 5.4 works well for particles of diameter above $\sim 50 \text{ \AA}$ (see *e.g.* Serpone *et al.*, 1995a). The reasonable congruence notwithstanding, there are other plausible explanations for the observed blue shifts in the bandgap. Studies by Serpone and co-workers (1995a, 1995b) contended that the earlier reports of blue-shifted absorption thresholds, taken as evidence for Q-size effects in small TiO_2 particles, may in fact be direct (Franck–Condon) electron transitions in an otherwise indirect-gap semiconductor.

Figure 5.3 shows absorption spectra of one of the three TiO_2 specimens of different sizes prepared from the hydrolysis of purified TiCl_4 arrested at different times for a concentration of *ca.* 15 g L^{-1} (Serpone *et al.*, 1995a). The spectra were identical with the absorption spectrum of bulk anatase TiO_2 and are in accord with the spectra of the $2R_{\text{part}} = 120 \text{ \AA}$ colloidal sols; the inset shows the spectral changes for the $133 \text{ \AA}$ specimen at concentrations ranging from 0.5 to 15 g L^{-1} . Note how the absorption onset seems to change with concentration. The diffuse reflectance spectra of the three dried specimens were identical with the spectrum in Fig. 5.3. For the TiO_2 sols examined, no aggregation took place at the higher concentrations. At a concentration of 15 g L^{-1} the absorption coefficient α was $\sim 1.9 \times 10^3 \text{ cm}^{-1}$ at 355 nm and $\sim 2.3 \times 10^2 \text{ cm}^{-1}$ at 375 nm. Treatment of these coefficients by the relationship for indirect-gap semiconductors, $\alpha_{(\text{hv})} \equiv (h\nu - E_g)^2$ (Pankove, 1975) gave two linear relationships with intercepts at $\sim 2.96 \text{ eV}$ and $\sim 3.22 \text{ eV}$. This implied that the three TiO_2 specimens examined were not size-quantised and that size quantisation must occur at sizes $2R_{\text{part}}$ much less than $\sim 20 \text{ \AA}$.

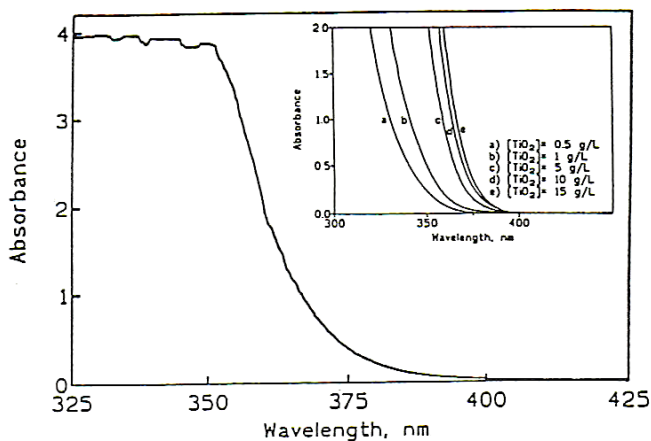


Figure 5.3 Absorption spectra of three TiO_2 specimens at a concentration of 15 g L^{-1} . Inset shows the concentration-dependent spectra of the $133\text{-}\text{\AA}$ sol. Reprinted with permission from Serpone *et al.* (1995a). Copyright (1995) American Chemical Society.

Figure 5.4 illustrates the determination of the bandgap energies and absorption thresholds for the three TiO_2 specimens, while Fig. 5.5 illustrates the absorption spectra and luminescence spectral envelope of the $23 \text{ \AA}$ particles (the excitation wavelength was 270 nm). The dashed lines are a qualitative delineation of the various emission components. The absorption edge in these spectra occurs at $3.64 \pm 0.04 \text{ eV}$, which was ascribed to a direct transition.

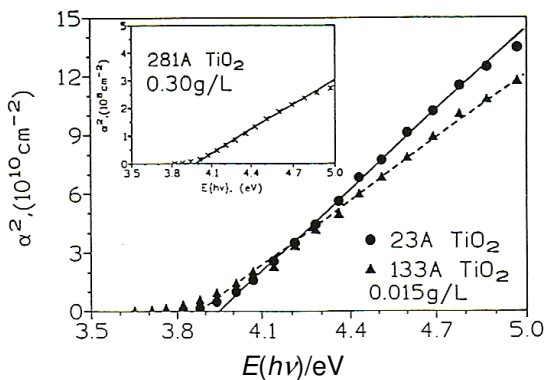


Figure 5.4 Plots of α^2 versus $E(h\nu)$ for three different sized titania specimens at the given concentrations. Reprinted in part with permission from Serpone *et al.* (1995a). Copyright (1995) American Chemical Society.

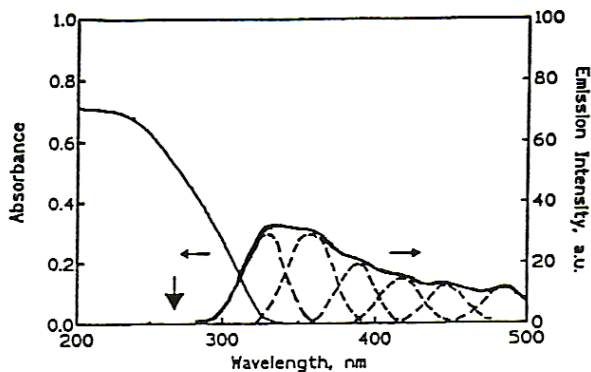


Figure 5.5 Absorption spectrum and luminescence envelope for the 23-Å TiO_2 particles at a concentration of 0.015 g L^{-1} . Reprinted in part with permission from Serpone *et al.* (1995a). Copyright (1995) American Chemical Society.

The attempt to describe the absorption coefficients by the $\alpha_{(\text{hv})} \equiv (h\nu - E_g)^2$ relationship for indirect-bandgap semiconductors failed to provide the expected linear correlation over the appropriate range of wavelengths. Linear correlation could only be observed from plots of the relation $\alpha_{(\text{hv})} \equiv (h\nu - E_g)^{1/2}$ (Pankove, 1975) that applies to direct-bandgap semiconductors. Figure 5.4 portrays the resulting treatment for the three sol specimens. Good linearity was evident at wavelengths below 340 nm (*i.e.* at energies greater than $\sim 3.9 \text{ eV}$). The stronger absorption features in Fig. 5.3 were best described as allowed direct band-to-band transitions in an otherwise indirect-bandgap semiconductor. The absorption threshold for this direct transition is 3.93 eV (for all three sols). The emission envelope confirmed the absorption results and evidenced additional transitions, albeit at energies lower than the bandgap energy (see Serpone *et al.*, 1995a). Emission bands at wavelengths longer than 400 nm (*i.e.* at energies smaller than $\sim 3.0 \text{ eV}$) indicate the presence of intragap surface states and shallow traps at energies less than $\sim 1.0 \text{ eV}$ below the conduction band. Specifically, they were observed at energies $0.40\text{--}0.64 \text{ eV}$ below the conduction band. Some of these surface states probably implicate oxygen vacancies (Lu *et al.*, 1994).

Radiative charge-carrier recombinations were examined by transient emission spectroscopy in the time window $0\text{--}7 \text{ ns}$ with excitation at 355 nm . Only emissions at wavelengths longer than 400 nm could be monitored by the streak camera used. Luminescence decay times for all three sols (loading of TiO_2 sols, 15 g L^{-1}) ranged from about 70 ps to 90 ps for the 23 Å and 281 Å colloids; the decay time for the 133 Å TiO_2 sol was $\sim 420 \text{ ps}$. These decay times and the corresponding emission

intensities implied that the luminescence quantum yield was largest for the 133 Å TiO_2 sol and less (but equal to each other) for the 23 Å and 281 Å colloidal sols.

Figure 5.6 illustrates the temporal evolution of the transient spectra of one of the sols examined, the 23 Å TiO_2 specimen, at various delay times after excitation with the 30 ps, 2.5 mJ laser pulse (Serpone *et al.*, 1995b). Subsequent to electron-hole pair formation and charge-carrier separation, in competition with recombination, a fraction of these carriers are trapped at lattice sites and some migrate to the surface in about 0.05–10 ps, depending on particle size, where they also get trapped to give Ti^{3+} species for the electron and $\{\text{Ti}^{4+}-\text{O}^{2-}-\text{Ti}^{4+}\}-\bullet\text{OH}$ for the hole (Lawless *et al.*, 1991).

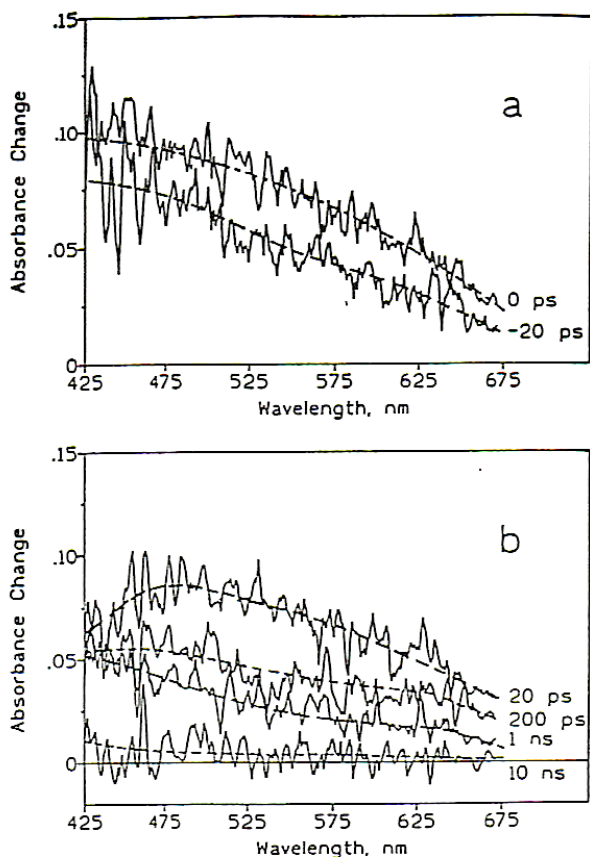


Figure 5.6 Transient absorption spectra at (a) -20 and 0 ps; and (b) at 20 and 200 ps, and 1 ns intervals after 30-ps pulse excitation of 23 Å TiO_2 colloidal particles in aqueous media (pH 2.7; loading 15 g L^{-1}). Reprinted with permission from Serpone *et al.* (1995b). Copyright (1995) American Chemical Society.

The 20 ps spectrum shows that the transients were fully developed by the end of the laser pulse. The absorption spectrum of the surface-trapped hole on TiO_2 shows a broad band at ~ 420 nm, whereas surface-trapped electrons showed broad absorption in the wavelength range 500–650 nm. From the evolution of the spectral features, it was inferred that the spectra of Fig. 5.6 represent composites of spectra of trapped holes and trapped electrons, with trapping occurring in less than *ca.* 1–10 ps. By 10 ns, there was little transient absorption observable except for a hint at the lowest wavelengths monitored (around 425–450 nm).

A femtosecond spectroscopic study by Colombo and co-workers (1995) on $2R = 20$ Å TiO_2 colloids indicated that trapping of electrons takes place in under ~ 500 fs; the fluence-dependent decay kinetics of trapped electrons showed a fast and a slow component. A global fit gave an electron–hole pair lifetime on the nanocluster of 23 ps. In the study by Serpone and co-workers (1995a, 1995b), the 23 Å colloid also showed biphasic decay kinetics for the transients, with the fast component being 240 ps and the slower component 10 ns. The inference that the charge carriers are trapped in such a short time has significant consequences in heterogeneous photocatalysis in the debate as to whether redox chemistry is initiated by free valence-band holes and conduction-band electrons, or by surface-trapped carriers.

Another interesting observation in the femtosecond study related to the extent of recombination at short times. Colombo *et al.* (1995) concluded from their study that by 30 ps about half of the charge carriers had recombined through a second-order process and that the longer-lived electrons are trapped in deep traps (or ejected) through a third-order Auger process. Our own studies (Lawless, 1993; Serpone *et al.*, 1995a, 1995b) indicated that by 10 ns nearly all (87–100%) photogenerated electrons and holes had recombined, depending on particle size.

The extent of this recombination at shorter time is summarised in Table 5.1. This prompted the realisation that the quantum yield of formation of surface redox species that initiate the redox chemistry in heterogeneous photocatalysis is probably around 10%. This conclusion is in accord with quantum yields of degradation of some substances reported elsewhere and with the quantum yield of $\sim 4\%$ for the formation of $\cdot\text{OH}$ radicals reported by Sun and Bolton (1995) for an Aldrich TiO_2 specimen illuminated at appropriate wavelengths.

Table 5.1 Summary of photophysical and spectral data for three TiO₂ specimens. From Serpone *et al.* (1995b).

Parameter	Data		
Size (diameter), Å	21	133	281
Volume, cm ³	4.85×10^{-21}	1.23×10^{-18}	9.97×10^{-18}
[TiO ₂], mol L ⁻¹	1.34×10^{-3}	5.26×10^{-6}	6.51×10^{-7}
<i>Transient emission decay</i>			
τ_e^1 , ps	67	405	66
τ_e^2 , ps	—	607	100
k_{em}^1 , s ⁻¹	1.5×10^{10}	2.5×10^9	1.5×10^{10}
k_{em}^{bulk} , cm ³ s ⁻¹	7.3×10^{-11}	3.1×10^{-9}	1.5×10^{-7}
<i>Transient absorption decay</i>			
τ , ps	483	120	38
k_r , M ⁻¹ s ⁻¹	0.6×10^{10}	3.9×10^{10}	10×10^{10}
k'_r , s ⁻¹	2.1×10^9	8.3×10^9	2.6×10^{10}
k_r^{bulk} , cm ³ s ⁻¹	1.0×10^{-11}	1.0×10^{-8}	2.6×10^{-7}
[e ⁻], mol L ⁻¹	2.8×10^{-4}	8.3×10^{-4}	9.8×10^{-4}
[e ⁻ /h ⁺] _{pairs} per particle*	0.2	157	1504
[e ⁻ /h ⁺] _v , cm ⁻³	4.12×10^{19}	1.28×10^{20}	1.51×10^{20}
Photons per particle	—	225	1811
% e ⁻ /h ⁺ pairs recombined			
by 20 ps	78	30	17
% e ⁻ /h ⁺ pairs recombined			
by 10 ns	100	87	93

* Laser fluence: $\sim 1.4 \times 10^{17}$ photons cm⁻².

5.2.2 Implications for photocatalysis

Two principal pathways have been recognised in the oxidation of organic and inorganic materials. One of these takes the surface OH⁻ group and/or H₂O molecules on the metal oxide TiO₂ as the primary target(s) for the reaction of photogenerated holes, a reaction which yields •OH radicals. The current view favours these •OH radicals as the primary oxidising entities. The alternative pathway sees the involvement of photogenerated holes in the direct oxidation of oxidisable substrates, a view

reinforced by the study by Draper and Fox (1990), which failed to detect any of the expected $\bullet\text{OH}$ -adduct intermediates following flash photolysis of several TiO_2 /substrate combinations.

Added to the question of what is the primary oxidising species, another issue that has challenged researchers is whether the primary oxidation event implicating $\bullet\text{OH}$ radicals takes place on the photocatalyst surface or whether $\bullet\text{OH}$ radicals desorb from the surface after their formation and react with the substrates in solution.

Of a more practical nature are the problems encountered in rendering and implementing metal-oxide photocatalysis as a viable technology in energy conversion and environmental remediation. One such issue is the fact that metal oxides such as TiO_2 absorb only about 3–5% of the solar radiation reaching the Earth's surface. This has led to the use of sensitisers to harness more solar wavelengths. Another issue was the early recognition that, to be a viable technology in environmental remediation, heterogeneous photocatalysis would necessitate shifting from metal-oxide aqueous slurries, which require an additional filtration step, to devices/reactors, to the case where the photocatalyst is immobilised onto some appropriate inert support.

Of a more fundamental nature is the issue that, once generated, electrons and holes tend to recombine fast; so their lifetimes are rather short to compete effectively with relatively slow redox chemistry occurring on the photoactivated TiO_2 surface or in the solution phase. Clearly the above issues needed some resolution.

5.2.3 The InterParticle Electron Transfer (IPET) process

To surmount the last issue, Serpone *et al.* (1984) introduced a novel strategy in photocatalysis: interparticle electron transfer between two coupled semiconductors to accomplish vectorial displacement of photoelectrons and photoholes. This strategy was first applied to the visible-light induced transformation of the noxious and toxic H_2S into a useful fuel (namely H_2), and to the photooxidation of alcohols by the Serpone/Pelizzetti/Grätzel collaborative groups (see references in Serpone, 1994a). Figure 5.7 illustrates the essence of the IPET process in a system containing both CdS and TiO_2 particles, in which the events are described by reactions 5.6 to 5.10 for the conversion of hydrogen sulphide.



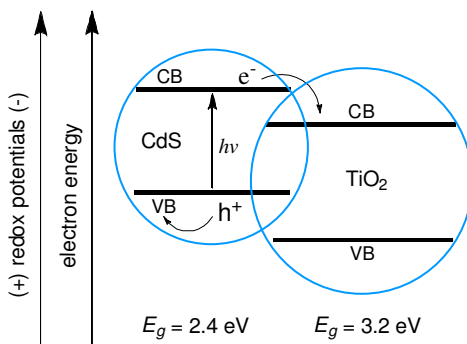
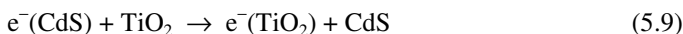


Figure 5.7 Scheme illustrating the vectorial displacement of an electron from the conduction band of CdS onto the conduction band of TiO₂.



Loading the TiO₂ semiconductor particles with a suitable redox catalyst (*e.g.* RuO₂) leads to a more efficient conversion of H₂S (~1%, rising to ~2% in the presence of SO₃²⁻ ions) and to hydrogen, a less harmful and more useful product. The combination of CdS and TiO₂ leads to a decrease of the electron–hole recombination process. Charge separation is achieved through the selective vectorial transfer of electrons from the conduction band of CdS into that of TiO₂. The transfer of holes is thermodynamically inhibited.³ An analogous process was observed in the photo-oxidation of alcohols (Serpone *et al.*, 1985b). The electron transfer underlying the IPET strategy has since been confirmed by photoelectrochemical, photoconductance, spectrofluorimetric and picosecond laser spectroscopic techniques (Serpone, 1994a).

Photoconductance studies carried out in collaboration with Pichat's group (Pichat *et al.*, 1988) showed that electron transfer can also take place between solid bulk phases of CdS and TiO₂. The occurrence of electron transfer, and its direction and extent, depended on the pretreatment and conditions of preparation of the two solid phases. In aqueous suspensions, the conduction band of CdS lies ~0.2–0.5 eV below that of TiO₂ and electron transfer occurs from CdS to TiO₂, its probability depending on the state of aggregation and interparticle collisions during the stirring stage. Under vacuum, however, electron transfer between the two solid phases takes place from TiO₂ to CdS, a remarkable and unexpected observation. This can only be possible if

³ Holes move spontaneously up on the (electron) energy scale and electrons move down.

the Fermi level of TiO_2 *in vacuo* is at higher energy than the Fermi level of the CdS system. This happens because illumination of the CdS– TiO_2 couple under dynamic vacuum causes ionosorbed oxygen to photodesorb from the surface of the TiO_2 particles, leaving excess electrons and shifting the Fermi level of TiO_2 below that of CdS (Pichat *et al.*, 1988).

IPET has also been demonstrated to occur in some reductive processes (Serpone, 1994a) and in the photooxidation of phenolic substrates on CdS, ZnO and TiO_2 suspensions. If these semiconductors are photoactivated when coupled to certain other metal oxides as acceptors, they become the electron donors (Serpone *et al.*, 1995c).

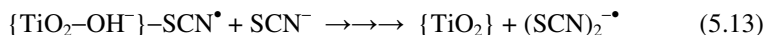
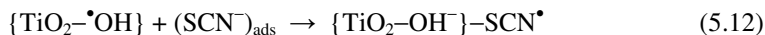
5.2.4 The nature of the valence-band hole

Chemical evidence supports the view that the $\bullet\text{OH}$ radical is the major oxidising species in the photooxidative mineralisation of organics. Such evidence includes the observation that hydroxylated intermediates are formed during photooxidation processes, and that these intermediates bear close resemblance to products obtained by oxidation with Fenton's reagent.⁴ However, this view has not met with universal acceptance. Difficulties in interpreting results regarding the nature of the photo-generated hole in light-activated TiO_2 were resolved by a study by Lawless *et al.* (1991) using pulse radiolysis, which enables the behaviour of one charge carrier to be examined without interference from the other. To assess the nature of oxidised TiO_2 particles, Lawless and co-workers examined the reaction of TiO_2 colloids with $\bullet\text{OH}$ radicals produced radiolytically by irradiation of N_2O -saturated aqueous solutions with high-energy electrons. The growth rate of the product, described simply as $\{\text{TiO}_2-\bullet\text{OH}\}$, varied linearly with TiO_2 loading, with a second-order rate constant of $6.0 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. This is a remarkably large value, greater than the conventional accepted diffusion-limiting rate constant for bimolecular reactions of 10^9 – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The second-order rate of decay of $\{\text{TiO}_2-\bullet\text{OH}\}$ increased linearly with the concentration of $\bullet\text{OH}$ radicals with a rate constant of $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

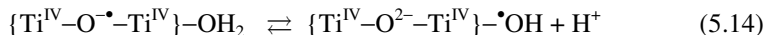
The optical spectrum of the $\{\text{TiO}_2-\bullet\text{OH}\}$ product showed an absorption onset at ~470 nm rising toward the UV and reaching a maximum at ~350 nm. Molecular oxygen had no effect on the fate of this product. However, the thiocyanate ion was oxidised by it, yielding the $\text{SCN}\bullet$ radical, which in the presence of excess SCN^- ions produced the dimeric anion radical $(\text{SCN})_2^{\bullet-}$. The rate of decay of $\{\text{TiO}_2-\bullet\text{OH}\}$ in the presence of thiocyanate occurred by two pathways: a SCN^- -independent path ($k =$

⁴ Fenton's reagent is a mixture of Fe^{2+} and H_2O_2 that contains abundant $\bullet\text{OH}$ radicals.

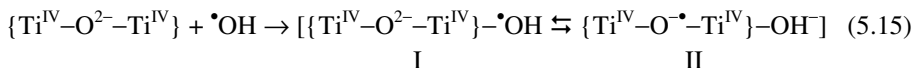
$5.4 \times 10^4 \text{ s}^{-1}$) and a SCN^- -dependent path ($k = 3.7 \times 10^5 \text{ s}^{-1}$). These rates are nearly identical to those of the reaction between light-activated TiO_2 and the thiocyanate ion, in which the hole was thought to oxidise the thiocyanate ions directly, in reactions analogous to reactions 5.11–5.13. Oxidation of SCN^- ions in the pulse radiolytic experiments occurred through the following sequence (Lawless *et al.*, 1991).



The electron transfer reaction 5.12 takes place between the SCN^- ion and the $\bullet\text{OH}$ radical when both are adsorbed at the surface of the same TiO_2 particle. Consideration of the yield of the radical dimer in reaction 5.13 permitted an estimate of the redox potential of the surface-bound $\bullet\text{OH}$ radical, $\{\text{TiO}_2-\bullet\text{OH}\}$, of about +1.5 V *vs.* SHE. It is therefore a strongly oxidising species, yet a rather deep hole trap, lying ~ 1.3 eV above the valence band of TiO_2 . The $\text{p}K_{\text{a}}$ of $\{\text{TiO}_2-\bullet\text{OH}\}$, as defined by reaction 5.14, was estimated to be 2.8–2.9.



Given that a photogenerated free hole reacts with water or OH^- groups on arrival at the TiO_2 surface to create, an adsorbed $\bullet\text{OH}$ radical, a process which occurs on a small particle within a few tens of picoseconds, it was not possible under the conditions of this study to distinguish between a trapped hole (species II in reaction 5.15) and an adsorbed $\bullet\text{OH}$ radical (species I).



The product of the $\bullet\text{OH}$ reaction with TiO_2 particles, $\{\text{TiO}_2-\bullet\text{OH}\}$, was therefore described as a trapped hole (adsorbed hydroxyl radical) and no distinction between I and II of reaction 5.15 could be made. It has also been suggested by Mićić and co-workers (1993a, 1993b) that the surface-trapped hole might be the deprotonated form $\{\text{Ti}^{\text{IV}}-\text{O}^{2-}-\text{Ti}^{\text{IV}}\}-\text{O}^\bullet$ of species I, at least at low temperatures.

Lawless *et al.* (1991) concluded that adsorbed $\bullet\text{OH}$ radicals (surface-trapped holes) are the major oxidising species in photocatalysis, while so-called *free* hydroxyl radicals (if there are any) play only a minor role. This makes sense: since the $\bullet\text{OH}$ radical reacts with TiO_2 at a diffusion-controlled rate, the desorption of $\bullet\text{OH}$ from the TiO_2 surface to the solution phase seems highly unlikely. The surface-trapped hole, as defined by reaction 5.15, accounts for most of the observations which had previously

led to the suggestion of the involvement of $\bullet\text{OH}$ radicals in TiO_2 photocatalysis. Formation of hydroxylated intermediate species and H_2O_2 can all occur via a surface reaction involving surface-bound $\bullet\text{OH}$ radicals.

Most significantly, these studies showed that the debate as to whether the oxidising species was the hole or the surface-bound $\bullet\text{OH}$ radical was pointless since these two are but one indistinguishable species. Yet the debate continues to this day, with many researchers continuing to distinguish between the two entities.

5.2.5 The nature of photocatalysis

We now turn to the meaning of the term 'photocatalysis'. We begin with catalysis as defined simply as a process in which a catalyst, Cat, accelerates a thermodynamically favoured but kinetically slow reaction, the catalyst being fully regenerated at the conclusion of the reaction. When photons are also involved in the reaction, the term *photocatalysis* has been used, without implying any specific mechanism, to describe the acceleration of a photoreaction by the presence of a catalyst. The catalyst may accelerate the photoreaction by interacting with the substrate in either its ground state or its excited state, and/or with the primary product. This definition is not explicit as to whether photons also interact with the catalyst. It also embraces photosensitisation, albeit such a process, officially defined (Glossary, 1985) as a photochemical change occurring in one molecular entity as a result of photon absorption by another molecular entity known as the photosensitiser, is not necessarily catalytic. In other words, the term photocatalysis has been taken as a general label to indicate that light and a substance (the catalyst or initiator) are necessary entities to increase the rate of the reaction shown schematically in eq. 5.16.



This broad description indicates the required reagents without undue constraints as to the (often unknown) mechanistic details of the chemical process. For the chemical reaction 5.17 involving molecules M of a substrate yielding product molecules P, there may be a corresponding catalytic process described by reaction 5.18.



The simplest description of catalysis is that addition of a catalyst (Cat) increases the rate at which equilibrium is reached in reaction 5.18, as compared with the

reaction 5.17. After a single act of the reaction (or completion of the reaction) the catalyst can be recovered in its original state, and in the same quantity as before the reaction. The reaction rate increases if the activation energy in the catalytic process (reaction 5.18) is lower than the corresponding energy in reaction 5.17, so clearly the reaction pathway in the catalytic process of reaction 5.18 is different from that in reaction 5.17. This description requires no prior knowledge of mechanism, although a more complex and precise description of any particular catalytic process would also show how the catalyst is intimately involved in the chemical steps.

In thermal (catalytic) reactions, changes in the electronic configuration of the system occur following the regrouping of nuclei or fragments without any transitions to electronic excited states. Transformation of chemistry to photochemistry occurs when a chemical reaction is induced by absorption of photons by some reagent M to yield a product P (reaction 5.19). The corresponding photocatalysed process is then given by reaction 5.20.



Unlike the thermal reaction 5.17, the photoreaction 5.19 occurs through an excited electronic state of the reagent(s), followed by the regrouping of the various nuclei or fragments. Typically, the photochemical reaction 5.19 is irreversible. If light is taken as a quasi-reagent in reaction 5.19 (as is often the case in mechanistic studies), the back reaction must then follow the pathway of reaction 5.21.



where $h\nu$ denotes photons of identical energy to those involved in the forward reaction 5.19. This reaction is however highly unlikely, so the back reaction $P \rightarrow M$ must proceed by a different pathway.

It is relevant to consider two different approaches to photocatalysis. The first sees the sequence $5.17 \rightarrow 5.18 \rightarrow 5.20$, that is, from chemistry (reaction 5.17) to catalysis (reaction 5.18) to photocatalysis (reaction 5.20). Photocatalysis is then catalysis of a thermal reaction (reaction 5.17) by an excited state of the catalyst produced as a result of light absorption by the catalyst. The role of light is to form the active (excited) state of the catalyst or to produce more active sites on the surface of the solid specimen (for a heterogeneous system) during photoexcitation. An example of such a process is the photoinduced isotope exchange of oxygen and hydrogen occurring on photogenerated surface hole centres ($\text{O}_2^{\bullet-}$) on metal-oxide semiconductors and dielectrics. Oxidation of organic compounds over TiO_2 particles is another example, if absorption of photons by TiO_2 generates the active state of the photocatalyst.

The second approach to photocatalysis is $5.17 \rightarrow 5.19 \rightarrow 5.20$ (chemistry $\rightarrow$ photochemistry $\rightarrow$ photocatalysis). In this case, there is catalysis of the photochemical reaction 5.19 with changes of the reaction pathway. The first step involves interaction of the catalyst with the reagent (light) to form an intermediate species (*e.g.* an excited state of the catalyst), which subsequently reacts with another reagent (molecule M) to form the final reaction product (P).

Salomon (1983) proposed that photocatalysis be classified into two distinct categories: (1) *catalysed photolysis*, and (2) *photogenerated catalysis*. In the former, either the nominal catalyst {T}, or the substrate {M}, or both, are in an excited state during the catalytic step. The latter involves only ground states of the catalyst {C} and the substrate {M} in the catalytic step, a step that is thermodynamically spontaneous (exergonic). A quagmire of labels, all based on specific mechanisms, appeared to describe photocatalytic processes, labels that ultimately caused only confusion since a specific label is useful only in so far as the mechanism is reliable, and until such time as it has not been revised/modified by more recent experimental observations. Table 5.2 shows some of Salomon's labels and indicates whether the relevant processes are catalytic or non-catalytic in photons. Figure 5.8 shows the general schemes proposed by Salomon for *catalysed photolysis* which are non-catalytic in photons, and Fig. 5.9 illustrates some cases of *photogenerated catalysis*, which are catalytic in photons.

Table 5.2 Salomon's classification of catalytic and non-catalytic processes.

PHOTOCATALYSIS	
<u>CATALYTIC IN PHOTONS</u>	<u>NON-CATALYTIC IN PHOTONS</u>
<i>Photogenerated catalysis</i> Photoinduced catalytic reactions Stoichiometric photogenerated catalysis*	<i>Catalysed photolysis</i> Catalysed photochemistry Catalysed photoreactions Sensitised photoreactions Photosensitised reactions Photoassisted catalysis Stoichiometric photogenerated catalysis* Substance-assisted(catalysed) photoreactions

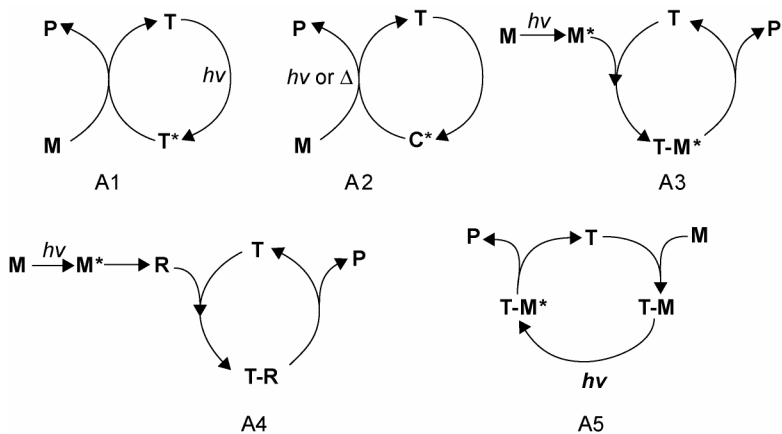


Figure 5.8 Schemes representing possible pathways for catalysed photolysis.

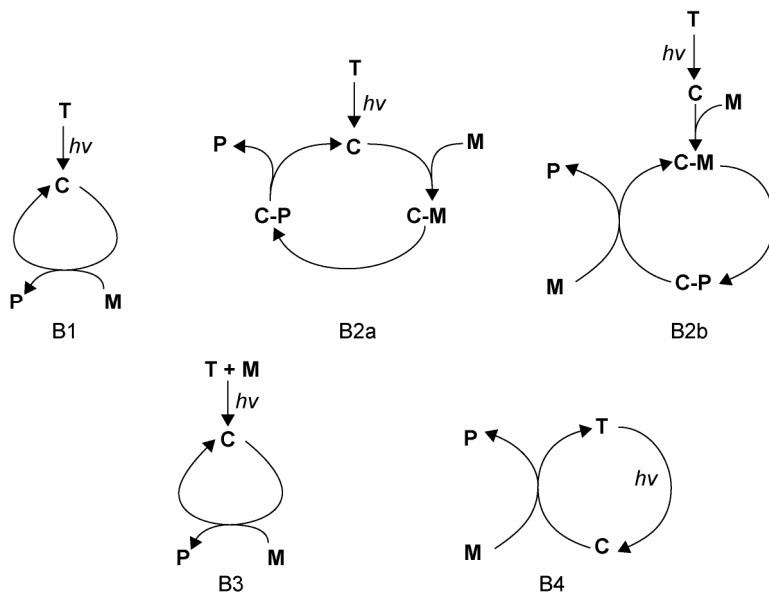


Figure 5.9 Schemes representing various pathways for the case of photogenerated catalysis.

This then begs the question what the role of the photons in photocatalysis is. Where in a given process the quantum yield is greater than unity, as often seen in reactions involving radicals, the process can be said to be *catalytic in photons*, and where the quantum yield is less than or equal to unity, the process may then be taken to be *non-catalytic in photons*.

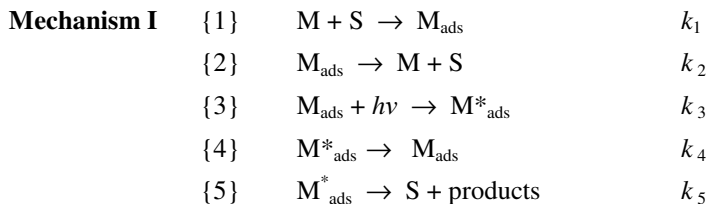
Note that the starred term *stoichiometric photogenerated catalysis* appears in both columns in Table 5.2 to indicate that it is a subcategory of *photogenerated catalysis* but is *not* catalytic in photons (B4 in Fig. 5.9 and A2 in Fig. 5.8 are identical). The term *stoichiometric* as used here signifies that a thermally active catalyst {C} interacts with the substrate {M} to regenerate the nominal catalyst {T} with each cycle of catalysis requiring the photolytic regeneration of {C}. Moreover, the distinction between an *assisted photoreaction* (turnover numbers less than unity) and a *catalysed photoreaction* (turnover numbers greater than unity) poses no difficulty in homogeneous (photo)catalysis since the turnover numbers can easily be estimated (also see below). However, that is not the case in heterogeneous (photo)catalysis, where a solid metal-oxide catalyst semiconductor or insulator is used to fulfil not only the role of light harvester, but also as the catalytic entity.

5.2.6 Turnover quantities

A definition of photocatalysis must be quite general to cover all particular processes (those considered above and no doubt many others) where there is an acceleration of a reaction with the participation of light. At the end of the reaction cycle, the photocatalyst is regenerated into its original state. In (thermal) catalysis, such kinetic parameters as turnover rate (TOR), turnover frequency (TOF) and turnover number (TON) are used to determine whether a given surface reaction is catalytic. Common processes to determine the corresponding kinetic parameters to demonstrate whether photocatalysis is catalytic have been considered by Serpone and co-workers (2000). At this juncture, the complexity of photocatalysis requires further consideration of *catalysed photolysis* and *photogenerated catalysis* in order to distinguish between the three turnover quantities.

In *catalysed photolysis*, a simple photochemical process (Mechanism I below) takes place on an inactive surface of the photocatalyst when light is absorbed by an adsorbed substrate. Stage {1} describes the adsorption of reagent M on a surface site S of the catalyst, and stage {2} desorption of adsorbed molecules M_{ads} . Both processes lead to the establishment of an adsorption/desorption equilibrium with equilibrium constant $K = k_1/k_2$. Stage {3} is photoexcitation of adsorbed molecules to

form an excited state M_{ads}^* , followed by the spontaneous decay of excitation (stage {4}) or chemical reaction (stage {5}) to regenerate the original state of the catalyst surface S, as required by the definition of catalysis. Otherwise, Mechanism I would simply describe a surface stoichiometric photoreaction. All the kinetic parameters (TOF, TOR, and TON) are determined under steady-state conditions in all Mechanisms I–III considered here, *i.e.* when the concentrations [M] and [S] and photon flow ρ are constant.



Introducing the quantum yield of product formation ϕ , and the equilibrium coverage θ of the catalyst surface by adsorbed molecules, where $\theta = [M_{\text{ads}}]/[S_0]$ in the dark at a concentration [M], the turnover quantities are given by eqs. 5.22–5.24 (Serpone *et al.*, 2000).

$$\text{TOF} \propto \phi k_3 \rho [M_{\text{ads}}] \quad (5.22)$$

$$\text{TOR} \propto \phi k_3 \rho \theta \quad (5.23)$$

$$\text{TON} \propto \phi t k_3 \rho \theta \quad (5.24)$$

where t is time. The TON yields information about ‘photocatalysis’ being catalytic, but the activity and efficiency of the photocatalytic process are better characterised by the quantum yield. The greater the quantum yield, the greater are the three turnover quantities. The same expression for the quantum yield is obtained for the photochemical reaction if M_{ads} is substituted with M, and M_{ads}^* with M^* in stages {3}–{5} of Mechanism I. The rate of such a photochemical process in homogeneous media (primed parameters) at the same concentration [M] is given by eq. 5.25.

$$\frac{dC}{dt} = \frac{k_3' k_5' \rho [M]}{k_4' + k_5'} \quad (5.25)$$

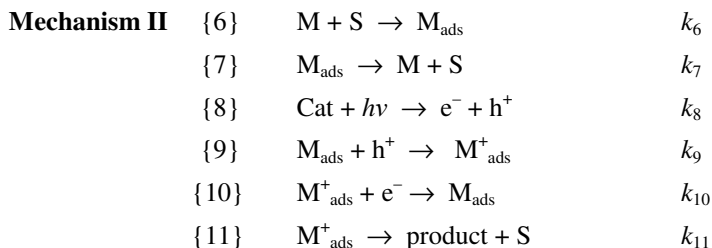
Thus acceleration of the photoreaction in a heterogeneous system (over a homogeneous one) occurs when changes in the structure of the adsorbed molecule cause an increase in (a) the photon absorption cross section, that is $k_3 > k_3'$, (b) the stabilisation of the excited state of the molecule $k_4 < k_4'$, and (c) a decrease of the activation energy

of the reaction $k_5 > k'_5$. Of course, the rate will also depend on the number of adsorption sites on the surface of the catalyst. The overall condition to observe acceleration is then given by

$$\frac{k_3 \phi}{k'_3 \phi} \frac{[M_{\text{ads}}]}{K[M]} \geq 1 \quad (5.26)$$

Consequently, if the absorption spectra of adsorbed and free molecules are similar (*i.e.* if $k_3 \approx k'_3$), then in order to observe photocatalytic acceleration the quantum yield of the heterogeneous photoreaction must be greater than the corresponding quantum yield of the homogeneous process, that is $\phi > \phi'$ (see eq. 5.26).

In the case of *photogenerated catalysis*, two different but equivalent models are worth considering: the Langmuir–Hinshelwood photocatalytic process and the Eley–Rideal photocatalytic process. The former is described by Mechanism II, in which the reaction occurs at a photochemically active surface when light is absorbed by the catalyst and leads to the generation of surface electrons (e^-) and holes (h^+).



Stages {6} and {7} are identical with stages {1} and {2} in Mechanism I above, and both processes lead to the establishment of an adsorption/desorption Langmuir-type equilibrium with constant $K = k_6/k_7$. Stage {8} is the photoexcitation of the catalyst, producing electrons and holes. Stage {9} describes carrier (hole) trapping by the adsorbed molecule to form a reactive radical state, whose decay occurs through recombination with an electron, as described by stage {10}. Stage {11} is the chemical reaction that yields the products and regenerates the original state of the catalyst surface, S. In this kinetic approach, the surface concentrations of holes and electrons for a uniform generation of charge carriers are given by eqs. 5.27 and 5.28

$$[h^+] = \alpha_h \rho \tau_h \quad (5.27)$$

$$[e^-] = \alpha_e \rho \tau_e \quad (5.28)$$

where α_h and α_e are the absorption coefficients of hole and electron absorption bands, ρ is the photon flow of the incident actinic light, and τ_h and τ_e are the lifetimes of holes and electrons, respectively. A disadvantage of the kinetic approach is that it assumes a spatially uniform generation of carriers in the bulk catalyst (*i.e.* $\alpha\rho = \text{const}$) and there is no diffusion limitation for carrier motion. A more detailed description uses a non-uniform generation of carriers. Such an expression for the concentration of surface carriers was reported earlier by Emeline *et al.* (1999a).

The process described by Mechanism II can be treated as a photochemical reaction on the surface of a solid (the catalyst Cat), whose role is to absorb light. Subsequent charge-carrier transfer to the adsorbed molecules produces an ionised state of the adsorbed molecules, as might also occur by direct interaction between the adsorbed molecules and light (not shown in Mechanism II). The excitation rate in Mechanism II, namely $k_9[h^+] = k_9\alpha_h\rho\tau_h$, is analogous to the rate $k_3\rho$ in Mechanism I. In mechanism II, the photocatalyst also takes part in the deactivation process such that $k_{10}[e^-]$ (or k_{10} for thermal ionisation of the adsorbed molecule) corresponds to k_4 in Mechanism I. Note that the 'light-inert' catalyst in Mechanism I also plays a role in the decay step (stage {4}) by changing the probability of deactivation.

In the current context, the turnover quantities are then given by

$$\text{TOF} = V\alpha\rho\phi \quad (5.29)$$

$$\text{TOR} = \frac{\alpha\rho\phi}{[S_O]} \times \frac{V}{s} \quad (5.30)$$

$$\text{TON} = t \frac{\alpha\rho\phi}{[S_O]} \times \frac{V}{s} \quad (5.31)$$

where V is the volume of the catalyst and s is the total surface area of the catalyst (Serpone *et al.*, 2000). Hence, just as in Mechanism I, all the turnover quantities are associated with the quantum yield of the photoprocess. Once again the activity and efficiency of the photocatalyst scale with ϕ .

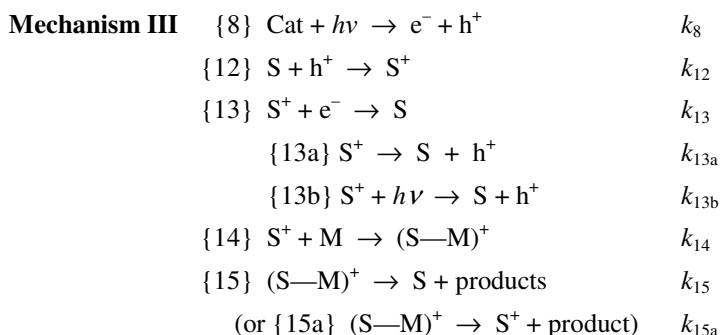
When free surface electrons and holes are the reactive centres (Volkenstein, 1987), the quantities TOR and TON are given by

$$\text{TOR} \propto \frac{k_6 k_9 k_{11} [M_{\text{ads}}]}{(k_{10} [e^-] + k_{11})} = \frac{V}{s} \tau_h \phi \quad (5.32)$$

$$\text{TON} = \left(\frac{tV\tau_h}{s} \right) \phi \quad (5.33)$$

In this case, catalysis occurs from the excited state of the catalyst and neither TOR nor TON depend on light irradiance, unless the decay of the ionised state of the adsorbed molecule is caused by recombination or photoionisation, and $k_{10}[e^-] \cong k_{11}$.

The Eley–Rideal heterogeneous photochemical process may be observed when the catalyst is photoexcited and no preadsorption of M occurs. This is described by Mechanism III.



As in Mechanism II, stage { 8 } corresponds to the photogeneration of free carriers. Stage { 12 } describes the trapping of carriers (in this particular case, holes) by surface defects (*i.e.* ‘potential’ surface-active centres) S to produce surface-active centres S^+ ; stage { 13 } denotes the ‘physical’ decay pathway of surface-active centres through recombination with charge carriers of the opposite sign, in this case electrons; this may also be a first-order thermal deactivation process (stage { 13a }) or a second-order photoionisation process (stage { 13b }). Stage { 14 } is a chemical reaction (chemisorption) which yields the intermediate species $(S-M)^+$ and is followed by secondary reactions to produce the photoreaction products (stage { 15 }).

The difference between stages { 15 } and { 15a } is worth noting. In stage { 15 } the original (ground) state S of the photocatalyst is restored ($\phi < 1$; the process is non-catalytic in photons), whereas in stage { 15a } the ionised state S^+ remains at the end of the reaction cycle ($\phi > 1$; the process is catalytic in photons). In the language of Salomon (1983), the former is *catalysed photolysis* and the latter is *photogenerated catalysis*. If the surface-active centres in *photogenerated catalysis* are the ionised states S^+ , then

$$\text{TOF} \propto \frac{dC}{dt}_s \quad (5.34)$$

$$\text{TOR} \propto \frac{dC/dt}{[S^+]_s} = k_{14}[M] \quad (5.35)$$

$$\text{TON} \propto t k_{14} [\text{M}] \quad (5.36)$$

As in the case of surface photochemical reactions (Mechanisms I and II), TON is greater than unity if turnover is determined for time $t < \tau$, where τ is the lifetime of the catalytic site. Hence the process can be said to be catalytic. It should be emphasised that TOR and TON are independent of light irradiance. They depend solely on reagent concentration, whereas the reaction rate and TOF behave differently, depending on light irradiance and (perhaps) on temperature for constant concentration of M. Indeed, as $k_{13} [\text{e}^-]$ (or k_{13}) $\rightarrow \infty$, then $d[\text{M}]/dt \rightarrow 0$ and $\text{TOF} \rightarrow 0$. The physical interpretation of this is that at high rates of 'physical' decay, *i.e.* when $k_{13} \rightarrow \infty$, the concentration of the active centres $[\text{S}^+] \rightarrow 0$, and so the reaction rate and TOF tend to zero. However, since TOR and TON are determined relative to a single centre, as soon as this centre becomes available the reaction cycle occurs and TOR and TON remain constant. Thus, TOR and TON reflect the activity of a given active centre (ionised state) S^+ but say nothing about the efficiency and activity of the catalyst. Moreover, for effective physical decay (*e.g.* at sufficiently high light irradiance), the rates of both processes [*photogenerated catalysis* (stage {15a}) and *catalysed photolysis* (stage {15})] become equal since they are determined only by the rate of photogeneration and (photo)decay of the ionised state; only one (or less than one) reaction cycle can occur during the lifetime of the active centre.

When we consider catalysis of a photochemical reaction and take light as one of the reagents, all the excited states of the catalyst (electrons, holes, and S^+ states) may be taken as intermediates of the catalytic photoreaction. The latter takes place by a different reaction pathway, in contrast to the original photochemical reaction. The original state of the catalyst S is restored at the end of the reaction, and the number of active centres is given by S_0 . This is analogous to thermal catalysis. For example, the oxidation or photooxygenation reaction of molecule M might follow the path



The reactive centre in such a process is neither the surface oxygen O_S nor the oxygen vacancy $\text{V}_\text{O}_\text{S}$, but rather some cluster corresponding to oxygen vacancies either with or without oxygen in the cluster. By analogy, in photocatalysis there are surface centres (defects), which can be in a state with trapped carriers (*i.e.* an intermediate, just like surface oxygen in the previous example) or without trapped carriers. These centres are in fact the centres of photocatalysis.

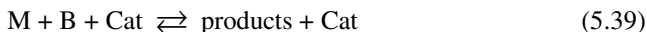
To complete the consideration of the previous examples, it is relevant to note that photogenerated catalysis (stage {15a}) does not require continuous irradiation since the excited state S^+ is reproduced at the end of each cycle. In this case, the excited state might be created during a pre-irradiation stage and there is no ‘physical’ decay during the course of the reaction. As a result, stages {12} and {13} can be excluded from this consideration in Mechanism III.

Even though the active (excited) state of the catalyst is restored in both *catalysed photolysis* and *photogenerated catalysis*, the kinetic parameters are different (Serpone *et al.*, 2000), since we deal with a different excited state of the catalyst, *i.e.* effectively we deal with different catalysts. Indeed, under irradiation the state of the catalyst (*e.g.* a semiconductor) may be characterised by the splitting of the Fermi level into two quasi-Fermi levels (in catalysed photolysis), whereas in photogenerated catalysis the state of the catalyst is characterised by a unique Fermi level (in the dark). This level may however be shifted compared with the original state of the catalyst because of the possibility of having different excited states after pre-excitation of the catalyst.

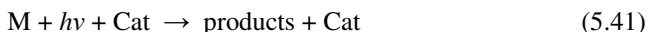
5.2.7 Further notions of photocatalysis

As implied above, there is nothing dramatically special about photocatalysis. It is simply another type of catalysis alongside, as it were, redox catalysis, acid–base catalysis, enzyme catalysis, thermal catalysis and others. Consequently, it is worth re-emphasising that any description of photocatalysis *must* correspond to the general definition of catalysis. This said, it could be argued that the broad label photocatalysis simply describes catalysis of a photochemical reaction.

To discuss this proposition further, we consider the following. If reaction 5.39 describes the catalysed reaction between reagent M and reagent B, then in the absence of the catalyst (Cat) we are left with the chemical reaction 5.40, which is no longer catalysed by Cat.



If this argument is carried further to the photocatalysed reaction 5.41, removal of the catalyst (Cat) leads to the photochemical reaction 5.42.



That is, we deal with catalysis of a photochemical reaction by the catalyst in its ground state. This notion is very important for determining the kinetic turnovers TOR and TON, since their evaluation requires knowledge of which state of the catalyst (*i.e.* which state of the surface-reactive centres) is being considered (Serpone *et al.*, 2000).

Some additional points are worth noting: (a) The photochemical reaction 5.47 takes place through the excited electronic state of the reagent, M^* , produced by light absorption by reagent M , unlike chemical reaction 5.40, which occurs through the ground states of the reagents M and B . In the photocatalysed process 5.41, the reaction takes place after electronic photoexcitation of either the catalyst (Cat) or the adsorbed molecules (M_{ads}), unlike catalysis which involves only the ground electronic states (albeit thermally excited vibrational states); (b) The photocatalysed reaction 5.41 and the photochemical reaction 5.42 describe irreversible processes, unlike thermal catalysis (reaction 5.39) and the thermal chemical reaction 5.40.

In a broad sense then, the label photocatalysis describes a photochemical process in which the photocatalyst accelerates the process, as any catalyst must do according to the definition of catalysis.

Photoexcitation of the catalyst changes the photochemical reaction pathway, which is typical of a catalytic process. It can also lead to changes in the spectral range of photoexcitation relative to the non-catalytic photochemical reaction (reaction 5.42) which, by analogy, can be considered as a change of the total activation energy because of the different reaction pathways in the catalytic process (reaction 5.39). Indeed, photoexcitation of the catalyst to form the excited state (Cat^* ; reaction 5.43) in reaction 5.41 is analogous to the formation of the intermediate adsorption complex (reaction 5.44) in thermal catalysis (reaction 5.39), both of which are followed by secondary steps with another reagent M .



Thus, just as in thermal catalysis (reaction 5.39) in which the adsorption complex is not the reactive centre, the excited state of the photocatalyst in the photocatalytic process 5.41 is also not a reactive centre but an intermediate. Consequently, to determine TOR and TON in the proposed Mechanisms I–III above one needs to consider as reaction centres the corresponding surface centres S in the *original state* of the photocatalyst and not S^+ or M_{ads}^* . As an example, we note the photocatalytic oxidation of organic compounds over TiO_2 in aqueous media. In this case, the ground state of S centres corresponds to the surface OH^- groups. It is these OH^- groups that are the catalytic centres, whereas the $\cdot\text{OH}$ radicals formed by hole trapping represent

intermediate species. Note also that the original S state of surface-active centres is restored after the reaction is completed. In the example of TiO_2 , this restoration or reconstruction of the original state of the catalyst is achieved by dissociative adsorption of water on the particle surface. In this context, photocatalysis (*i.e.* catalysed photolysis) is catalysis of a photochemical reaction by the original ground state of the catalyst prior to photoexcitation.

At this time, it is appropriate to reflect further on the principal difference(s) between *photogenerated catalysis* and *catalysed photolysis*. As implied earlier, any photochemical reaction (5.42) starts from light absorption by a reagent M to form an excited state of the molecule, M^* .



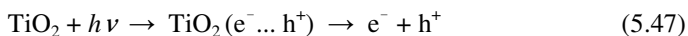
There always exists a physical pathway (radiative and/or nonradiative) for relaxation of the M^* state back to the ground state (reaction 5.46).



Accordingly, there is always a competition between chemical and physical pathways for decay of excited states. If the chemical pathway is inefficient, then the physical pathway will lead to relaxation of M^* to its ground electronic state M.

The same holds for *catalysed photolysis*. Indeed, since catalysed photolysis refers to catalysis of a photochemical reaction, there is a physical pathway for decay of the system back to its ground state. If the photocatalytic process occurred through photoexcitation of the catalyst, physical decay may occur through recombination, and/or through thermal and photoinduced ionisation of the excited state of the surface centres, which ultimately lead to regeneration of the original state of the catalyst. There is no such process in photogenerated catalysis. In the latter case, the state of the catalyst does not have a physical decay pathway and is the same before and after the reaction as in any thermal catalytic reaction. Note also that the catalytic process in photogenerated catalysis is reversible, unlike the case of catalysed photolysis.

On the basis of the above discussion, in its most simple description photocatalysis implies a catalysed process preceded by absorption of a photon by a material acting as the catalyst. Where the photocatalyst is a semiconductor nanoparticulate system, *e.g.* TiO_2 , which is the material treated in most detail in this chapter, absorption of photons of energy greater than 3.2 eV (for anatase; 3.0 eV for the rutile polymorph) leads to formation of conduction-band electrons and valence-band holes, which subsequently diffuse to the particle surface in competition with bulk recombination.



At the surface, these carriers are trapped by defect sites, surface states or oxidising or reducing agents. They are then poised to initiate redox chemistries with other substrates. A simple illustration of the complex sequence of events is shown in Fig. 5.10, which is a modification of the scheme of Fig. 5.2 to emphasise other steps in the overall process sequence. The trapped electron reduces the pre-adsorbed acceptor A to A^- , and the trapped hole oxidises the pre-adsorbed electron donor D to D^+ ; these are followed by other secondary steps.

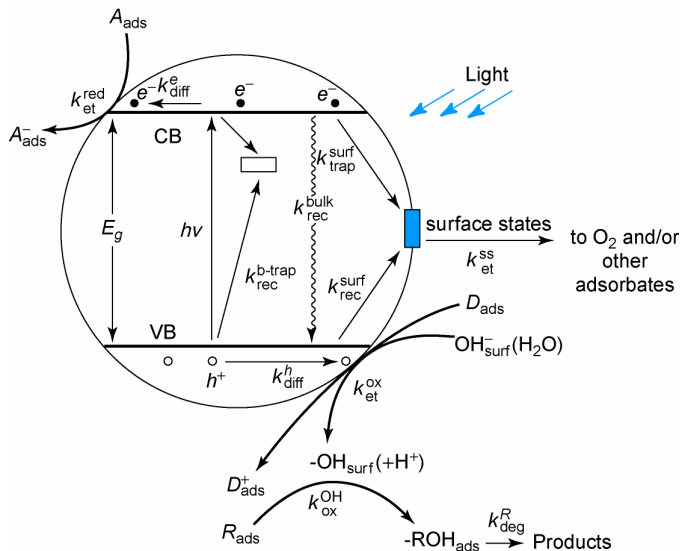
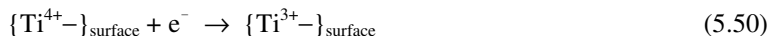
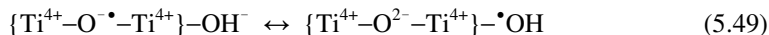
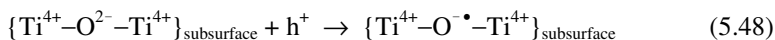
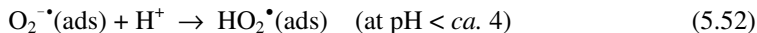


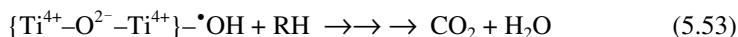
Figure 5.10 Scheme illustrating some important events that might take place on a metal-oxide particle subsequent to light absorption by the particle.

The acceptors and donors need to be pre-adsorbed at the surface to allow the slower chemistry to compete effectively with the ultrafast electron-hole recombination at the surface (Serpone *et al.*, 1995b). In a real TiO_2 dispersion, the donor is typically OH^- and/or H_2O , and the acceptor is the ubiquitous O_2 molecule, which is reduced to produce $\bullet\text{OH}_{(\text{ads})}$ radicals and the hydroperoxy radical, $\text{HO}_2\bullet_{(\text{ads})}$ (reactions 5.48 and 5.49, and 5.51 and 5.52). The surface Ti^{3+} species imparts a blue colour to the TiO_2 particles in the presence of hole scavengers in oxygen-free dispersions.



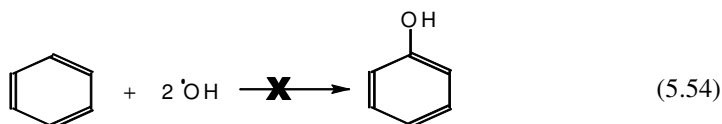


The $\bullet\text{OH}$ radical has the greater oxidation potential—*e.g.* in homogeneous aqueous phase $E^\circ = +2.8$ V vs. SHE for $\bullet\text{OH}$ and 1.7 V for $\text{HO}_2^{\bullet}$ radicals (Legrini *et al.*, 1993)—and the surface-bound $\bullet\text{OH}$ radical (reaction 5.53) is considered the primary oxidising agent in condensed media, at least at low concentrations of organic pollutant RH. This mechanism, however, has not been without debate (also see below for gas/solid systems).

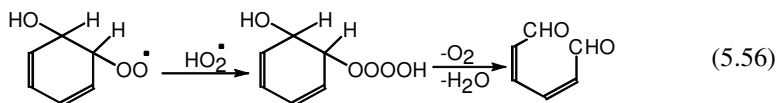
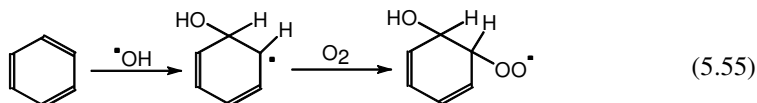


Besides acting as an electron scavenger, the precise role of O_2 has been elusive for some time and continues to be a subject of some debate. In several studies on the photocatalysed oxidation of aliphatic hydrocarbons, alcohols, ketones, carboxylic acids and aldehydes, Heller (1995) concluded that molecular O_2 , and not the photo-generated hole or $\bullet\text{OH}$ radical, is the primary oxidising agent. As evidence, data were given that photooxidation of *n*-octane films on water produced only traces of octanols.

In the case of benzene films the expected phenol was not produced (reaction 5.54), even though the $\bullet\text{OH}$ radical was initially involved to yield a radical species that is subsequently attacked by O_2 to produce a phenyl hydroperoxide.



Further reaction with the $\text{HO}_2^{\bullet}$ radical (reactions 5.55 and 5.56) gave a hydro-tetraoxide that decomposed to dialdehydes and/or to dicarboxylic acids. In aliphatic hydrocarbons, the $\bullet\text{OH}$ radical first abstracts a hydrogen atom from the chain. Subsequent addition of O_2 and further reaction with the hydroperoxy radical from reaction 5.52 led to formation of ketones and aldehydes (reactions 5.55 and 5.56; Heller, 1995).



5.3 Metal-oxide photochemistry, photophysics and modelling

Thus far we have described some of the features of heterogeneous photocatalysis that normally suffice for carrying out studies in environmental remediation using this particular Advanced Oxidation Process (AOP). Our interest, however, has also been focused on the properties of the metal-oxide photocatalysts, in particular TiO_2 and ZrO_2 . Specifically, we hoped to elucidate the details of photochemical and photophysical events occurring at the particle surface and in the lattice of the metal oxide. To achieve further understanding, we resorted to modelling the events that begin with photon absorption to obtain parameters with which we could interpret experimental data, and perhaps predict how experimental conditions could be modified to achieve greater efficiency and selectivity in photoreductive and photooxidative processes.

Among countless photoinduced processes, we focused on those photochemical processes that occur at the interface of solid/liquid and solid/gas heterogeneous systems, and on their relationship(s) with photophysical processes in solids.

The first step of any photostimulated process is photoexcitation of the system resulting from absorption of photons. In a heterogeneous system, the solid is typically responsible for light absorption. The photon energy in the near-UV/visible spectral region corresponds to the energy of excitation of the electronic subsystem(s) of the solid. Several types of photoexcitation of solids can be distinguished. The first is *intrinsic* photoexcitation, which leads to electron transitions from the valence band to the conduction band of the solid, or to formation of excitons (bound electron-hole pairs) when the excitation energy coincides with the excitonic absorption band of the solid. This type of photoexcitation corresponds to the fundamental absorption of solids, *i.e.* band-to-band (*intrinsic*) absorption.

5.3.1 Photoinduced processes in solids

In the ideal case of a perfect lattice structure, *intrinsic* absorption of light is the only excitation decay in an ideal solid, which return the solid to its initial ground state, are band-to-band e^-/h^+ recombination or excitonic decay (Fig. 5.11a). When the solid is an integral component of a heterogeneous system, interfacial transfer of charge carriers becomes possible. This is synonymous with the well-known three-level photochemical system shown in Fig. 5.11b. The pathway corresponds to a simple stoichiometric heterogeneous photoreaction. However, if the energy diagram of Fig. 5.11b were expanded to a four-level system (Fig. 5.11c), where the charge carrier cycle is now closed by redox reactions with both acceptor and donor molecules at the

surface, leading to complete relaxation of the solid back to the ground state, the process could then be viewed as being photocatalytic. Thus, any stoichiometric surface photoreaction can be considered as an incomplete photocatalytic cycle. The result of such an incomplete cycle is that at the end of the reaction the system goes into a new, higher energy state. An example of such a process is the photoinduced adsorption of molecules on metal-oxide surfaces.

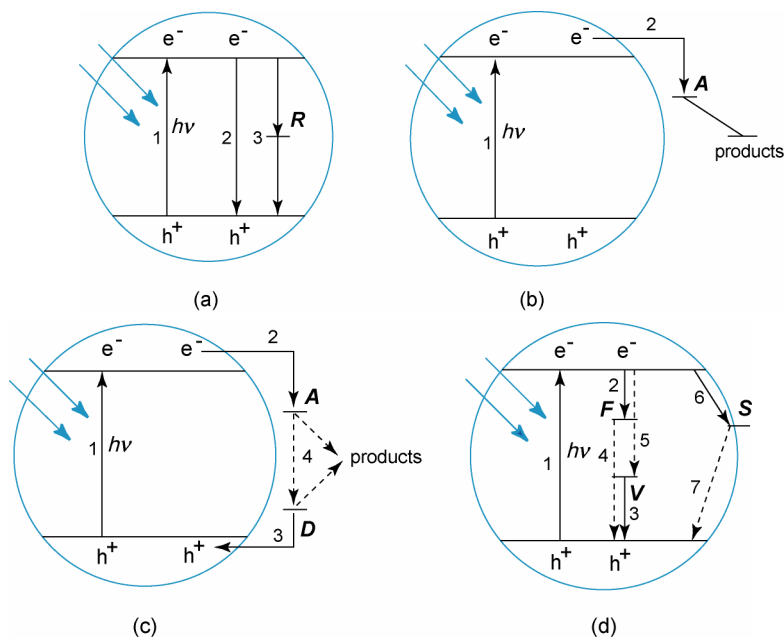


Figure 5.11 Schemes of excitation processes and relaxation in heterogeneous systems containing solid particles. (a) Step 1: photoexcitation; step 2: complete relaxation in ideal solids (band-to-band recombination); step 3: complete relaxation in real solids (free charge-carrier recombination through defect centres, R). (b) Step 1: photoexcitation; step 2: interfacial electron transfer from the solid to the acceptor molecule (stoichiometric reaction, incomplete relaxation). (c) Step 1: photoexcitation; step 2: interfacial transfer electron from the solid to the acceptor molecule; step 3: interfacial electron transfer from donor molecules to the solid to complete solid relaxation and the photocatalytic cycle; step 4: secondary chemical process to close the cycle of the charge carriers. (d) Step 1: photoexcitation; step 2: electron trapping by defect sites to form F -type colour centres (incomplete relaxation); step 3: hole trapping by defect centres to form V -type colour centres (incomplete relaxation); steps 4 and 5: slow recombination process through colour centres to complete the relaxation of the solid; step 6: electron trapping by surface defects to form surface-active (colour) centres, S, (incomplete relaxation); step 7: deactivation of surface-active centres through recombination (complete relaxation). Reprinted with permission from Emeline *et al.* (2005b). Copyright (2005) American Chemical Society.

Two well-known surface stoichiometric photochemical reactions can be identified: (i) the photostimulated adsorption of O_2 (reduction of acceptor molecules), and (ii) the photostimulated adsorption of H_2 (oxidation of donor molecules) on a metal-oxide surface. Both result in a new state of the heterogeneous system with charged species adsorbed on the solid. If these two processes occurred simultaneously they would yield a reaction identifiable as the photocatalysed oxidation of hydrogen to water. Nonetheless, such a simple mechanism gives but a small indication of the real processes that take place on solids and at interfaces of heterogeneous systems. We examine these cases later after a discussion of the nature of solids and a description of the photochemical/photophysical events taking place in these complex materials.

5.3.2 Nature of solids

No solid is perfect and none possesses an ideal lattice structure. Even for an ideal solid, its surface interrupts the translational symmetry of the lattice and consequently disturbs the periodic potential of the solid, leading to the creation of so-called regular surface states. Typically these surface states have different energy distributions compared with the distribution of defects in the bulk. They display their own absorption bands caused by specific surface absorption, with the energy of the photons absorbed being typically smaller than in the fundamental absorption (Fig. 5.11d). The result of surface absorption of light is formation of surface free electrons and holes, or of surface excitons, which can participate in redox surface reactions just as much as the charge carriers generated in the bulk do after their migration to the surface.

Surface reconstruction and surface relaxation processes can lead to changes in the energy distribution of carriers, and even to formation of a new structure of the solid in the subsurface space. Adsorption of molecules on the surface also changes the charge-carrier and energy distribution at the surface. All these events result in a new charge and energy distribution in subsurface space (*i.e.* the space-charge layer), which typically manifests itself as band bending in semiconductors.

Despite advanced methods of crystal growth, solids still contain lattice defects at concentrations around 10^{13} – 10^{14} cm^{-3} , and typical concentrations of defects and impurities in commercial samples are around 10^{18} cm^{-3} . The latter concentration is usually much greater than the concentration of photogenerated free charge carriers in solids under moderate photoexcitation. Consequently, defects are expected to play an important role in photoexcitation and relaxation processes in heterogeneous systems. In fact, defects create a local distortion of the periodic potential in the solid's lattice.

This leads to the appearance of local energy levels within the bandgap, which themselves lead to changes in the optical and electronic properties of solids.

Defects often play a dual role during photoexcitation of solids (Fig. 5.12). First, their presence, together with surface states, causes *extrinsic* absorption of light at energies much lower than the bulk bandgap (Emeline *et al.*, 1998a, 1998b). Depending on the type of defects and the mechanism of their photoexcitation, *extrinsic* absorption also leads to photoinduced generation of electrons and holes (Ryabchuk and Burukina, 1991; Emeline *et al.*, 1998a, 1998b, 2000a). Second, lattice defects can serve as carrier traps in charge-carrier recombination and the formation of photoinduced defects (colour centres). Carrier decay occurring through lattice defects is a more efficient process than band-to-band recombination since there is no limitation from charge-carrier momentum conservation, and the system's energy conservation rule is more easily satisfied. Carrier trapping by pre-existing defects causes the formation of new photoinduced defect states, or generation of a new type of defects, which leads to a new energy distribution of charge carriers in solids.

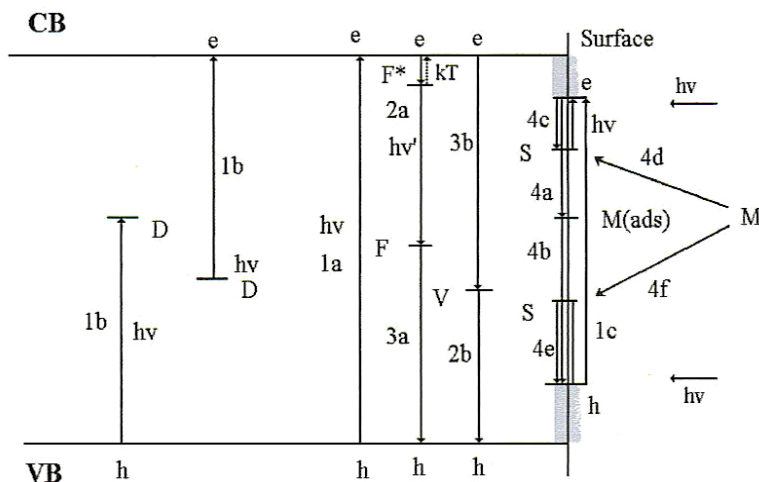


Figure 5.12 Summary of processes of photoexcitation and relaxation in solids as a part of a heterogeneous system. 1a – intrinsic (band-to-band) photoexcitation corresponding to the fundamental absorption of solid; 1b – extrinsic photoexcitation of bulk defects (D) in solids leading to generation of free carriers; 1c – photoexcitation of intrinsic and extrinsic surface states generating surface charge carriers; 2a, b – charge-carrier trapping by bulk defects to form colour centres; 3a, b – recombination of free charge carriers with carriers trapped by colour centres; 4a, c – free charge-carrier trapping by deep and shallow surface traps (surface defects) to form surface active centres; 4b – recombination between free charge carriers and carriers trapped by surface-active centres; 4e – thermoactivated deactivation of surface-active centres; 4d, f – chemical interaction of molecules with electron and hole surface-active centres.

5.3.3 Photophysical events in solids

Photogenerated colour centres differ from each other by the energy distance E_d between the level of the trapped carrier within the energy bandgap of the semiconductor (or of the insulator) and the bottom of the conduction band for electron centres, and the top of the valence band for hole centres (see Fig. 5.12 for details). From this viewpoint, a given photogenerated centre can be described as a shallow centre (or trap) if the energy of the trapped carrier E_d is comparable with the energy of thermal excitation of the crystal lattice (*i.e.* if $E_d \approx kT$), or as a deep energy centre (trap) if $E_d \gg kT$. The difference between the various types of photogenerated centres is determined by the dominant decay pathway that brings the solid back to its initial state (without any trapped carriers). In general, any photoinduced centre can lose a carrier as a result of: (i) thermal ionisation, with a thermal quenching probability given by q_{th} ; (ii) recombination with a charge carrier of the opposite sign, for which the recombination probability is q_{rec} ; (iii) photoionisation caused by incident photons, q_{ph} ; and (iv) tunnelling recombination of adjacent hole and electron centres, q_{tun} . The total probability q of decay of these centres is then given by eq. 5.57.

$$q = q_{th} + q_{rec} + q_{ph} + q_{tun} \quad (5.57)$$

Following the work of Siline and Trukchin (1985) for the simplest case of centres with one trapped carrier, the kinetics of their formation typically follow an exponential growth and approach the steady-state concentration of photoinduced defects N_d as given by

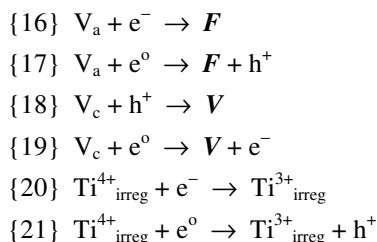
$$N_d = N_o \left(\frac{p}{p + q} \right) \quad (5.58)$$

where N_o is the number of pre-existing defects of a given type, p is the probability of photocarrier trapping defined, as are the corresponding quenching probabilities q , as the number of events per unit time. For shallow traps, thermal ionisation usually dominates; that is, $q_{th} \gg q_{rec} + q_{ph} + q_{tun}$. In contrast, thermal ionisation can be neglected for deep energy centres, *i.e.* $q_{th} \ll q_{rec} + q_{ph} + q_{tun}$. In the latter case, centres that have a high ability to capture a carrier of the opposite sign, *i.e.* those for which $q_{rec} \gg p$, can serve as effective recombination centres. These centres do not accumulate in considerable quantity in illuminated crystals. At the same time, recombination centres are mainly responsible for the concentrations of photogenerated carriers in wide-bandgap solids because direct band-to-band recombination is rather inefficient compared with recombination involving deep energy centres. Contrasting recombination centres, deep energy centres, for which $q_{rec} \sim p$, do accumulate in sufficient

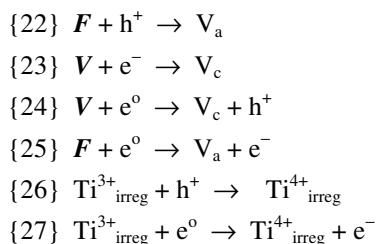
amount in solids under illumination. Such defects are the colour centres because they usually have absorption bands located in the UV/visible regions of the spectrum and determine the lasting stable colour of pre-illuminated, initially colourless wide-bandgap solids (see Figs. 5.11d and 5.12). Photoionisation of colour centres by the incident actinic light may, to some extent, reduce the colour saturation level under illumination when $q_{\text{rec}} \approx q_{\text{ph}}$. An increase in temperature causes an increase of the probability q_{th} for the thermal ionisation of colour centres, which *de facto* may become the dominant pathway for the decay of colour centres.

The processes of formation and decay of photoinduced centres under steady-state photoexcitation conditions, as well as under picosecond laser pulse excitation have been examined (Sahyun and Serpone, 1997; Emeline *et al.*, 1998a, 1998b, 1999b, 2000a). The spectra of colour centres induced were examined under steady-state irradiation of ZrO_2 and Sc_2O_3 , *in vacuo* and in the presence of oxygen or hydrogen.

Figure 5.13 illustrates the temporal evolution of photoinduced colour centres in colloidal TiO_2 following picosecond laser pulse excitation. These centres form as a result of carrier/exciton trapping by pre-existing defects (anion V_a and cation V_c vacancies), and by some ions in irregular (defect) positions in the lattice, for example $\text{Ti}^{4+}_{\text{irreg}}$ in titania (or $\text{Zr}^{4+}_{\text{irreg}}$ in zirconia)—stages {16} to {21}.



The kinetics of formation of colour centres under steady-state irradiation show that, after a period of growth, the concentration of the colour centres (F , V and $\text{Ti}^{3+}_{\text{irreg}}$ in the case of TiO_2) reaches steady state, as determined by the competing processes of formation and decay of the colour centres—stages {22}–{27}.



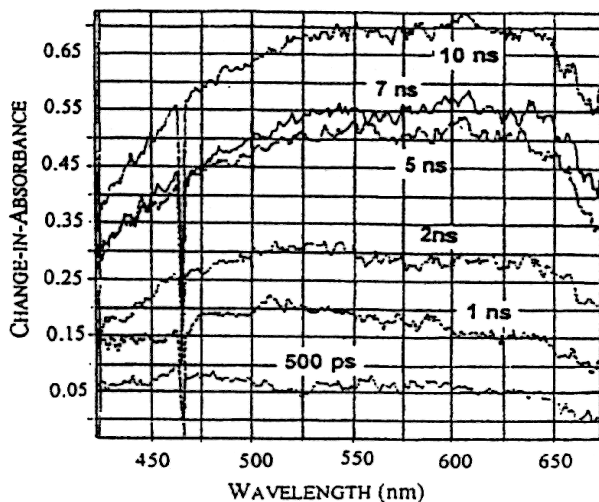


Figure 5.13 Absorption spectra of photoinduced colour centres in colloidal TiO_2 formed after picosecond laser pulse excitation. Reprinted with permission from Sahyun and Serpone (1997). Copyright (1997) American Chemical Society.

The same processes, stages {16}–{21} and {22}–{27}, occur after the solid is photoexcited by picosecond laser pulses. Figure 5.14 shows the time evolution of photoinduced electron centres, Ti^{3+} , in TiO_2 . The difference between pulse-induced and steady-state processes for the formation of colour centres lies in the different probabilities of formation and decay of the centres, which dictate the different time

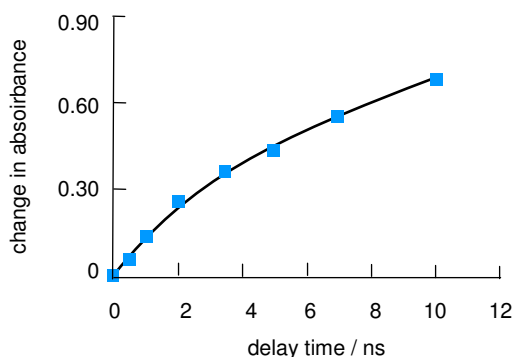


Figure 5.14 Kinetics of Ti^{3+} -type colour centres formation in colloidal TiO_2 after picosecond laser pulse excitation. Adapted with permission from Sahyun and Serpone (1997). Copyright (1997) American Chemical Society.

evolution and time scales of the relevant processes. First, a disparity in the excitation irradiance causes the concentration of photogenerated charge carriers to be different. For steady-state irradiation at moderate light intensity, the carrier concentration is much smaller than the defect concentration, whereas under laser pulse excitation the concentrations of charge carriers and defects may be comparable. Second, during steady-state irradiation, *F*- and *V*-centres (see stages {16}–{18}) form such that steady-state irradiation will also activate these centres, unlike the case of laser pulse excitation, where irradiation encounters only the original pre-existing defects on the metal oxide particles. For example, in the original state before laser pulse excitation, there exist only anion and cation vacancies, so only processes of charge-carrier trapping are possible. This means that any faster process (either electron or hole trapping) occurs first, with a probability dictated by the trapping cross-section of the relevant vacancy and the mobility of the relevant carriers; this is followed by slower processes of trapping and recombination of charge carriers of the opposite sign. By contrast, under steady illumination all these processes may occur simultaneously, since some photogenerated colour centres will have been formed during irradiation. Lifetimes of carriers and photoinduced centres assessed by time-resolved laser techniques may therefore not correspond to those found under steady-state conditions.

The rates of recombination of free holes with *F*-centres (trapped electrons; stage {22}) and free electrons with *V*-centres (trapped holes; stage {23}) are slow compared with those occurring at recombination centres R. Ordinarily, R centres are also deep-energy carrier traps that can later capture carriers of both signs. These processes can also be expressed by quasi-chemical reactions (not shown) similar to stages {16}, {17} and {22}, {23}. The distinction between colour centres and recombination centres lies in the trapping efficiency of the second carrier. Colour centres (small rate constants for stages 4a and 4b, or small cross sections of second carrier trapping) accumulate in dielectrics in amounts comparable to those for primary defects (V_a and V_c in the present notation). By contrast, the ultimate concentrations of recombination centres R^- and R^+ (in the charged states corresponding to *F*- and *V*-centres, respectively) are much smaller than the concentration of R because of the large cross sections in the trapping of the second carrier. In this description, intrinsic defects as well as impurities can serve as primary defect species for both colour and recombination centres, depending on the peculiarity(ies) of their interaction with free carriers. In other words, the process of colouration of solids may be taken as an incomplete recombination through the defects when trapping of the second carrier is not fulfilled. Note the analogy between colouration (as incomplete recombination) and recombination on the one hand, and surface stoichiometric photochemical reaction and photocatalysis on the other. The difference between these two pairs of

processes is that the photocatalytic process closes the external charge-carrier cycle, whereas the recombination process results in the complete internal charge carrier cycle. To support this analogy, photoprocesses of defect formation can also be considered as a reduction or oxidation of *intrinsic* or *extrinsic* pre-existing defect sites. Indeed, electron trapping by some defects (*e.g.* by Ti^{4+} to form Ti^{3+}) can be designated as a reduction process, whereas hole trapping to produce such hole centres as the $\text{O}^{\bullet-}$ radical anion state localised at a negatively charged defect in a metal-oxide lattice can be described as photooxidation of oxide O^{2-} anions. Also, according to the electronic theory of catalysis (Baru and Volkenstein, 1978), any adsorbed molecule is a surface defect and can act as a carrier trap just as much as *intrinsic* lattice defects do in the bulk of the solid. Adsorbed species such as the localised $\text{O}_2^{\bullet-}$ anion radical formed through electron trapping by O_2 is one such defect. In terms of defect formation, the interaction of $\text{O}_2^{\bullet-}$ anion radicals with photoholes at the TiO_2 surface, which leads to photodesorption of O_2 molecules (Lu *et al.*, 1994; Linsebigler *et al.*, 1995) or dissociation of the $\text{O}_2^{\bullet-}$ anion radical into oxygen atoms, as proposed by Formenti and Teichner (1978), can be characterised as recombination decay of photoinduced centres. Clearly, there is competition between physical (internal) and chemical (external) pathways for the system to relax after photoexcitation.

Irradiation of solids *in vacuo* leads to formation of photoinduced colour centres (see Figs. 5.13 and 5.14). Those photoinduced centres formed at the surface can serve as reactive centres for surface chemical processes: *V*-centres ($\text{O}_s^{\bullet-}$) serve as reactive centres for oxidative reactions with donor molecules, whereas electron *F*-type centres or low-coordinated metal ions with trapped electrons (Ti^{3+} for TiO_2 and Zr^{3+} for ZrO_2) lead to a reductive reaction with acceptor molecules.

Figures 5.15 and 5.16 show absorption changes caused by adsorption of donor (H_2) and acceptor (O_2) molecules on pre-irradiated samples corresponding to the absorption spectra of surface-active (colour) centres. These are long-lived because they are deep traps, and consequently the probability of their thermal ionisation is very low, *i.e.* $q_{\text{th}} \rightarrow 0$. After irradiation, the probabilities of photoionisation q_{ph} and of recombination decay q_{rec} are both zero since there are no free charge carriers left in the solid. Thus, the total probability of centres decaying is also zero (eq. 5.57). These centres are responsible for the 'memory' effect, whereby pre-irradiation of solids causes consequent dark reactions. However, under irradiation the recombination probability for the decay of colour centres on the surface and in the bulk is not 0, that is $q_{\text{rec}} \neq 0$. If solids are excited in their fundamental absorption band, the probability of photoionisation of active (colour) centres may be negligible compared with the recombination probability, that is $q_{\text{ph}} \ll q_{\text{rec}}$. Thus, under irradiation the active states of surface defects have a limited lifetime to initiate surface chemical reactions.

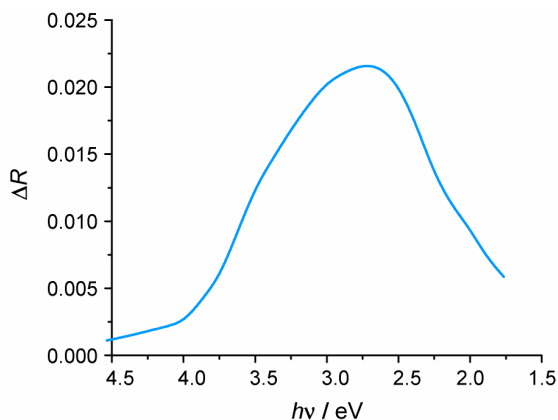


Figure 5.15 Absorption spectrum of long-lived surface-hole-active centres on powdered Sc_2O_3 particles. Note that change in reflectance ΔR is equivalent to absorbance A of the colour centres. Adapted with permission from Emeline *et al.* (1999c). Copyright (1999) American Chemical Society.

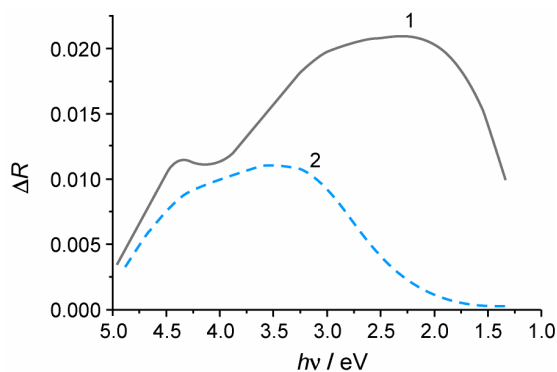
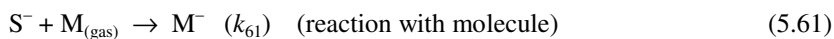
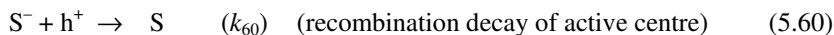
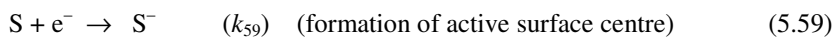


Figure 5.16 Absorption spectrum of long-lived surface electron (1) and hole (2) active centres on ZrO_2 particles. Adapted in part with permission from Emeline *et al.* (1998b, 2000a). Copyright (1998, 2000) American Chemical Society.

To summarise what has been said above, the following series of reactions of surface photochemical processes can occur:



Formation of surface-active (colour) centres occurs via capture of free electrons and holes by the surface traps S. For completeness, creation of electron active centres S^- is indicated in reaction 5.59 (k_{59}). The centres interact with molecules M to yield the intermediate species M^- (reaction 5.61, k_{61}). Reaction 5.60 describes the recombination pathway for the decay of surface-active centres.

In the quasi-stationary approximation ($d[S^-]/dt = 0$; $d[e^-]/dt = 0$; and $d[h^+]/dt = 0$), the rate of the photochemical reaction $d[M]/dt$ can be expressed in terms of steady-state surface concentrations of photoelectrons $[e^-]$ and photoholes $[h^+]$:

$$-\frac{d[M]}{dt} = \frac{k_{59}k_{61}[S][e^-][M]}{k_{60}[h^+] + k_{61}[M]} \quad (5.62)$$

A more detailed expression for the surface concentration of charge carriers can be obtained by assuming that the steady-state concentration of photoelectrons and photoholes is given by eqs. 5.63 and 5.64.

$$[e^-] = \alpha\rho\tau = g\tau_e \quad (5.63)$$

$$[h^+] = \alpha\rho\tau_h = g\tau_h \quad (5.64)$$

where g denotes the volume rate ($\text{cm}^{-3} \text{s}^{-1}$) of generation of charge carriers and α is the absorption coefficient (cm^{-1}). Taking into account eqs. 5.63 and 5.64, eq. 5.62 can be transformed to a form (eq. 5.65) that summarises the dependence of the reaction rate on photon flow ρ and the concentration of reagent $[M]$:

$$\left(-\frac{d[M]}{dt}\right)_{\rho, [M]} = \frac{\alpha\rho[M]}{\beta\rho + \gamma[M]} \quad (5.65)$$

where the coefficients α , β and γ are independent of ρ and $[M]$. Equation 5.65 describes the experimental dependencies of the phenol photodegradation rate in TiO_2 dispersions on photon flow and phenol concentration (Emeline *et al.*, 2000b), and of the photostimulated adsorption rate of O_2 on ZrO_2 particles on oxygen pressure and photon flow (Emeline *et al.*, 1998a); these are shown in Fig. 5.17.

Equation 5.65 can be cast into a Langmuir–Hinshelwood form when the photon flow ρ is constant. It can be used to describe all the experimental dependencies of the reaction rate on photon flow. In fact, when $\beta\rho \ll \gamma[M]$, eq. 5.65 gives the linear dependence on light intensity observed in studies by Emeline and co-workers (1998a) and Basov *et al.* (1977). When $\beta\rho \gg \gamma[M]$ the reaction rate is independent of photon flow (Ollis, 1991). In other cases, when $\beta\rho$ is comparable to $\gamma[M]$, the dependence of the reaction rate on photon flow is sub-linear; at certain ratios between these two

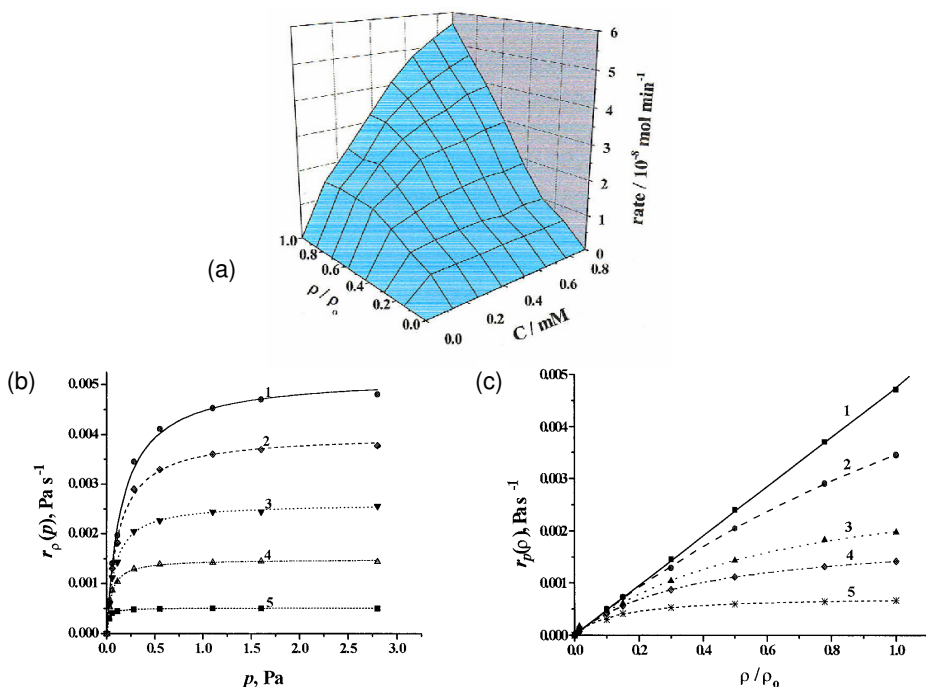


Figure 5.17 (a) Three-dimensional dependence of the rate of phenol photodegradation in illuminated aqueous TiO_2 dispersions on the concentration of phenol and the photon flow of the actinic light; (b) Dependencies of initial rates of oxygen photoadsorption on ZrO_2 , $r_p(p)$, on pressure p at different photon flow ($\rho_0 = 1 \times 10^{15} \text{ photons cm}^{-2} \text{ s}^{-1}$): (1) $\rho = \rho_0$; (2) $\rho = 0.78 \rho_0$; (3) $\rho = 0.5 \rho_0$; (4) $\rho = 0.3 \rho_0$; (5) $\rho = 0.1 \rho_0$; (c) Dependencies of initial rates of oxygen photoadsorption on ZrO_2 as $r_p(p)$ on photon flow ρ {as ρ/ρ_0 } at different initial oxygen pressures: (1) $p = 2.8 \text{ Pa}$; (2) $p = 0.28 \text{ Pa}$; (3) $p = 0.11 \text{ Pa}$; (4) $p = 0.055 \text{ Pa}$; (5) $p = 0.028 \text{ Pa}$. The straight line corresponds to the first-order process dependence on photon flow. Reprinted in part with permission from Emeline *et al.* (2000b), Copyright (2000) Elsevier Science S.A.; and in part from Emeline *et al.* (1998a), Copyright (1998) American Chemical Society.

terms the dependence may be similar to the square-root dependence reported by Emeline *et al.* (1998a, 2000b). Thus, rate dependencies on light intensity and on concentration of reagent are in fact interdependent. The reason for such behaviour is that the physical pathway (internal cycle, Fig. 5.11d) for decay of system excitation through recombination involving surface-active (colour) centres competes with the chemical pathway (external cycle, Figs. 5.11b and 5.11c) involving chemical interactions between molecules and surface-active centres. Indeed, at sufficiently high concentrations $[M]$, or at low light intensity (*i.e.* for $\beta\rho \ll \gamma[M]$), recombination through surface-active centres is completely shut down and the reaction rate is

determined only by the rate of formation of the active centres (reaction 5.59), which depends directly on light intensity. By contrast, at high light intensity or at low concentrations of M (*i.e.* for $\beta\rho \gg \gamma[M]$), the recombination process through surface-active centres dominates, and the reaction rate is then directly proportional to the concentration. Obviously, at high concentrations, when the physical recombination of charge carriers through surface-active (colour) centres is completely shut down, the probabilities of all other physical pathways of decay are altered. This will have a particular effect on colouration processes.

5.3.4 Deposition of silver clusters on TiO_2 particles

The conclusion of competition between the physical recombination pathway through surface-active centres and surface chemical reaction is supported by time-resolved spectroscopic data for the photocatalytic deposition of silver on nanoparticulate TiO_2 in a solid/liquid heterogeneous system that consists of TiO_2 particles and silver acetate (Sahyun and Serpone, 1997). The system was excited by picosecond laser pulses in the presence of high concentrations of alcohol pre-adsorbed on the particle surface. The alcohol served as an effective hole scavenger to prevent recombination decay of photoinduced surface-active (colour) centres Ti^{3+} (stage {26}). As a result, dependencies of the concentration of photoinduced surface-active centres Ti_s^{3+} and the concentration of reaction product Ag^0 formed during the reductive interactions with surface-active sites (reaction 5.66) on the energy of the laser pulse were linear (as shown in Figs. 5.18 and 5.19). The extent of absorption by Ag^0 is independent of the concentration of Ag^+ ions in solution. This implies that the recombination of holes

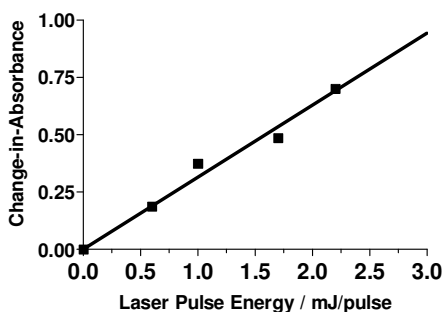


Figure 5.18 Dependence of the amount of the laser pulse-induced surface-active centres Ti_s^{3+} on laser pulse energy. Adapted with permission from Sahyun and Serpone (1997). Copyright (1997) American Chemical Society.

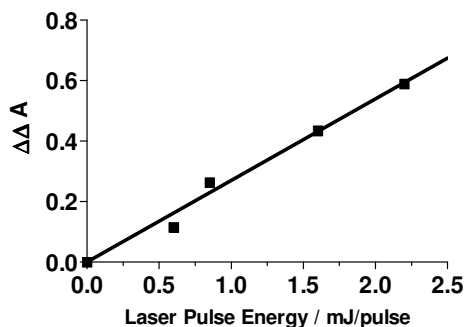
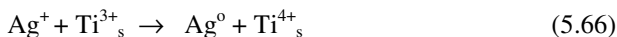


Figure 5.19 Dependence of the amount of photoreduced silver Ag^0 on laser pulse energy. Adapted with permission from Sahyun and Serpone (1997). Copyright (1997) American Chemical Society.

with Ti^{3+} (stage {26}) is shut down by effective hole scavenging by the alcohol, and the lifetime of surface-active centres is then long enough to permit the centres to react with any amount of Ag^+ used in the experiments if $[\text{Ag}^+] \geq 5 \times 10^{-5} \text{ M}$.



This assumption is strongly supported by the kinetics of formation of Ti^{3+} species (see Fig. 5.14) as no decay through recombination was observed.

5.3.5 Charge conservation in solids

The charge conservation law requires that the concentration of electrons and holes trapped in colour centres during irradiation *in vacuo* under steady-state conditions (since the concentration of free charge carriers can be neglected compared with that of trapped carriers) or after irradiation must be equal. That is

$$[F_o] = [V_o] \quad (5.67)$$

Then, in the presence of high concentration of donor molecules D at the interface, when recombination through surface hole centres is shut down, the charge conservation law requires that

$$[F_D] = [V_D] + [D^{+\bullet}] \quad (5.68)$$

where $[D^{+\bullet}]$ is the concentration of cation radicals formed by donor molecules with trapped holes, and $[F_D]$ and $[V_D]$ are the concentrations of electron and hole colour centres, respectively, in the solid in the presence of donor molecules.

At high concentrations of acceptor molecules A, expression 5.67 transforms into

$$[F_A] + [A^{\bullet-}] = [V_A] \quad (5.69)$$

where $[A^{\bullet-}]$ is the concentration of anion radicals formed by acceptor molecules with trapped electrons, and $[F_A]$ and $[V_A]$ are the concentrations of electron and hole colour centres in the solid. From eqs. 5.67–5.69, we see

$$[F] + [A^{\bullet-}] = [V] + [D^{+\bullet}] \quad (5.70)$$

For the general case of a complete photocatalytic cycle, taking the difference between eqs. 5.70 and 5.67 yields expression 5.71.

$$\Delta[F] + [A^{\bullet-}] = \Delta[V] + [D^{+\bullet}] \quad (5.71)$$

where $\Delta[F]$ and $\Delta[V]$ denote the difference in concentration of colour centres caused by surface chemical reactions compared with those *in vacuo* when only the physical (internal) pathway of excitation decay takes place. Consequently, eq. 5.71 can be expressed differently as

$$r_{\text{ox}} + \frac{d[V]}{dt} = r_{\text{red}} + \frac{d[F]}{dt} \quad (5.72)$$

where r_{ox} and r_{red} are the rates of surface oxidation and reduction reactions, respectively, and $d[V]/dt$ and $d[F]/dt$ are the rates of hole and electron trapping by defects. Equation 5.72 reflects the competition between internal and external cycles of the relaxation in heterogeneous systems. Expectations from eqs. 5.67–5.72 are illustrated by some experimental results (Emeline *et al.*, 1998c, 1999c, 2000a) summarised in Figs. 5.15 and 5.16 for the processes of formation of colour centres during photoexcitation in the fundamental absorption band of solids in solid/gas (and solid/liquid) heterogeneous systems.

Another illustration of the competition between chemical and physical pathways can be made on the basis of photobleaching of colour centres. Absorption bands of photoinduced colour centres formed during the photoexcitation of solids are typically red-shifted for up to a few eV compared with *intrinsic* or *extrinsic* absorption bands.

In summary, photoexcitation can lead to photoionisation of colour centres and consequent generation of free charge carriers that can participate in both physical and chemical processes. The spectral limits of photochemical and photophysical processes are red-shifted in photocoloured solids compared with their initial states. Thus, photocolouration leads to spectral sensitisation of solids in heterogeneous systems (Ryabchuk and Burukina, 1991; Emeline *et al.*, 1998a, 1998b, 1999c).

5.3.6 Photoexcitation of colour centres

The probability of photoionisation of colour centres is either comparable to or greater than the probability of recombination decay. The fate of free charge carriers generated from the photoionisation of colour centres is the same as in previous considered cases (stages {16}–{21} and {22}–{27}, and reactions 5.59–5.61). Analysis of the kinetics and the mechanism of photobleaching yields for electron colour centres: **F**

$$\left(\frac{d[F]}{dt} \right)_A - \left(\frac{d[F]}{dt} \right)_{\text{vac}} = - \left(\frac{d[A^\cdot]}{dt} \right) \quad (5.73)$$

$$\left(\frac{d[F]}{dt} \right)_{\text{vac}} - \left(\frac{d[F]}{dt} \right)_D = - \left(\frac{d[D^+]}{dt} \right) \quad (5.74)$$

and similarly for hole colour centres:

$$\left(\frac{d[V]}{dt} \right)_{\text{vac}} - \left(\frac{d[F]}{dt} \right)_A = - \left(\frac{d[A^\cdot]}{dt} \right) \quad (5.75)$$

$$\left(\frac{d[V]}{dt} \right)_D - \left(\frac{d[V]}{dt} \right)_{\text{vac}} = - \left(\frac{d[D^+]}{dt} \right) \quad (5.76)$$

These equations correspond to eq. 5.72 and describe the experimental kinetics of photobleaching shown in Fig. 5.20. From the experimental data and the relationships between colouration and surface chemical processes described by eqs. 5.73–5.76, it is possible to estimate the quantum yields of photobleaching processes and of surface photochemical reactions for solid/gas heterogeneous systems involving ZrO_2 and Sc_2O_3 . Experimental ϕ values of photobleaching of **F**-centres in ZrO_2 are (*in vacuo*) $\phi_{F(\text{vac})} = 0.32 \pm 0.03$; in the presence of oxygen in the gas phase $\phi_{F(\text{O}_2)} = 0.52 \pm 0.04$; and in the presence of hydrogen $\phi_{F(\text{H}_2)} = 0.22 \pm 0.03$. The quantum yields of photo-stimulated adsorption of O_2 and H_2 during the photoexcitation of colour centres are $\phi_{\text{O}_2} = 0.16 \pm 0.02$ and $\phi_{\text{H}_2} = 0.11 \pm 0.02$, respectively.

The relationship between measured quantum yields considering dissociative adsorption of H_2 on surface hole centres can be presented in the form of eqs. 5.77 and 5.78, in complete accord with eqs. 5.73 and 5.74.

$$\phi_{F(\text{O}_2)} - \phi_{F(\text{vac})} = \phi_{\text{O}_2} \quad (5.77)$$

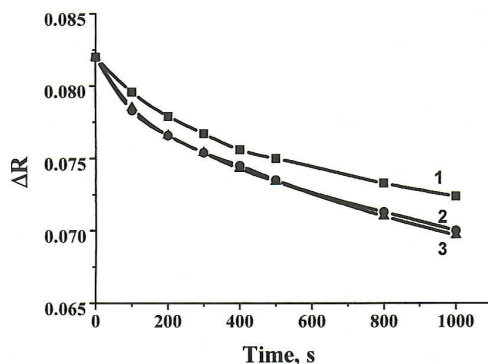


Figure 5.20 Temporal decay of absorbance (as ΔR) vs. irradiation time, illustrating the photobleaching of V-type colour centres in Sc_2O_3 (1) *in vacuo*; (2) in the presence of dihydrogen; and (3) in the presence of CO. Reprinted with permission from Emeline *et al.* (1998c). Copyright (1998) American Chemical Society.

$$\phi_{F(\text{vac})} - \phi_{F(\text{H}_2)} = 2\phi_{\text{H}_2} \quad (5.78)$$

The same is true for the heterogeneous system involving Sc_2O_3 photoexcited in the absorption band of V-type hole colour centres. The quantum yield of photobleaching of V-type colour centres is $\phi_V = 0.022 \pm 0.002$ *in vacuo*, and $\phi_V = 0.046 \pm 0.003$ in a reducing (H_2 or CO) atmosphere. The quantum yield of the photostimulated adsorption of dihydrogen and carbon monoxide on coloured scandia is $\phi = 0.023 \pm 0.002$, so that the ϕ of photobleaching of hole colour centres in H_2 (or CO) reflects the sum of the quantum yields of photobleaching of colouration *in vacuo* and the surface photochemical processes. That is,

$$\phi_{V(\text{H}_2)} - \phi_{V(\text{vac})} = \phi_{\text{H}_2} \quad (5.79)$$

Ionisation of photoinduced colour centres can also be caused by an increase in temperature, which increases the probability q_{th} of the thermostimulated decay of colour centres (see eq. 5.57). Thermoionisation and photoionisation of colour centres generate free charge carriers, which can also participate in both physical and chemical processes. Figures 5.21 and 5.22 show some examples and their correlations. The former depicts the temperature dependencies of the decay of V-type hole colour centres in Sc_2O_3 and the extent of hydrogen adsorption. Note that H_2 adsorption is not observed in non-coloured samples (Emeline *et al.*, 1999b). Figure 5.22 illustrates the temperature dependence of thermostimulated emission and the rate of thermostimulated adsorption of H_2 on MgAl_2O_4 . The dependencies are caused by the appearance of holes on the surface generated from the thermal ionisation of hole colour centres (reactions 5.80 and 5.81).

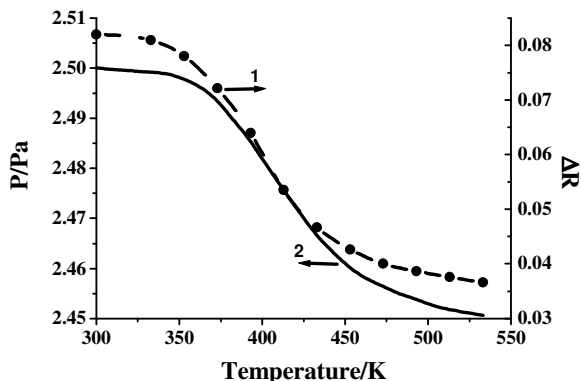


Figure 5.21 Temperature dependence of the absorption (as ΔR) of (1) V-type colour centres in Sc_2O_3 , and (2) the thermostimulated adsorption of dihydrogen shown as a drop in pressure P in the gas phase. Reprinted with permission from Emeline *et al.* (1998c). Copyright (1998) American Chemical Society.

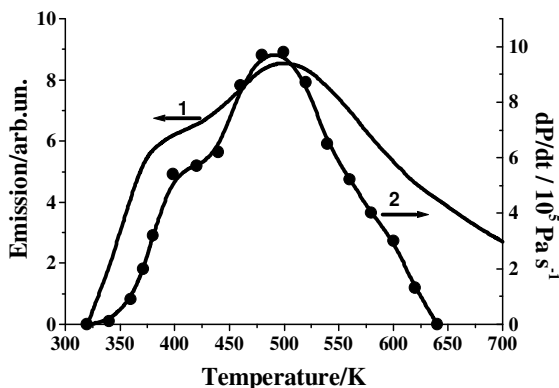


Figure 5.22 Temperature dependencies of (1) the thermostimulated emission and (2) the rate of the thermostimulated adsorption of dihydrogen on MgAl_2O_4 . Reprinted with permission from Emeline *et al.* (1999c). Copyright (1999) American Chemical Society.



Similar effects were observed for the heterogeneous systems $\text{MgAl}_2\text{O}_4/\text{H}_2$ and ZrO_2/O_2 , for which a correlation between the rate of thermostimulated adsorption and the intensity of thermostimulated luminescence could be established (Fig. 5.22; Ryabchuk and Burukina, 1991; Emeline and Ryabchuk, 1998; Emeline *et al.*, 1999c).

In this case, the thermostimulated luminescence is caused by free charge-carrier trapping that accompanies emission of photons (reaction 5.82).



Again, this physical process 5.82 competes with the chemical process of reaction 5.81. In the ZrO_2/O_2 heterogeneous system, the thermal destruction of electron colour centres is responsible for the appearance of free electrons that participate in both thermoluminescence and oxygen adsorption processes. To summarise, all the processes considered above are displayed in some detail in the scheme of Fig. 5.23 in terms of bulk processes (b) and surface processes (s).

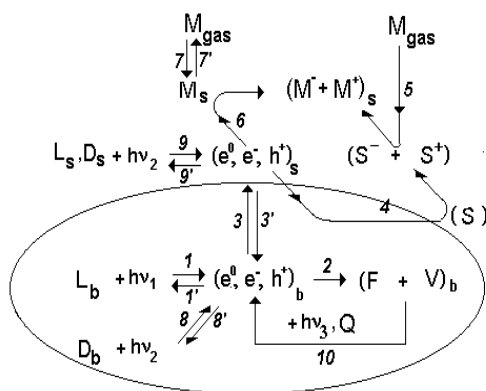


Figure 5.23 Scheme summarising some of the photostimulated processes in a heterogeneous system containing a wide-bandgap solid. D denotes a defect, L the lattice and the subscripts b and s refer to bulk and surface respectively.

Bulk processes

1. *Intrinsic* photoexcitation of the bulk lattice L_b (fundamental absorption of light with photon energy $h\nu_1 \geq E_g$) leads to generation of free electrons (e^-) and holes (h^+), or excitons (e^0) (step 1).
2. *Extrinsic* photoexcitation of pre-existing bulk defects D_b by light with photon energy $h\nu_2 < h\nu_1$ also leads to generation of free electrons and holes (step 8).
3. Trapping of free charge carriers and excitons by bulk defects form colour (F - and V -type) centres (step 2) in the bulk.
4. Photobleaching ($h\nu_3$) and thermo-annealing (Q) of colour centres leads to generation of free electrons and holes (step 10).

5. Band-to-band recombination of free charge carriers and exciton decay (step 1'), and recombination and exciton decay through defects (step 8') are probably accompanied by luminescence.
6. Free carrier and exciton exchange between the bulk and the surface from diffusion and/or drift of these carriers (steps 3 and 3').

Surface processes

1. Light absorption ($h\nu$) by (regular and irregular) surface states L_s and D_s leads to generation of surface free charge carriers and surface excitons (step 9).
2. Charge-carrier and exciton trapping by pre-existing surface defects (S) yields surface-active centres (S^- and S^+) for adsorption and catalysis (step 4).
3. Interaction of molecules in the gas (or liquid) phase, M_{gas} , with surface-active centres initiates surface chemical processes (step 5; Eley–Rideal mechanism).
4. Adsorption and desorption of molecules in the gas (or liquid) phase (steps 7 and 7') lead to adsorption/desorption equilibria.
5. Interaction of surface charge carriers and excitons with pre-adsorbed molecules (M_s) initiates a surface reaction (step 6; Langmuir–Hinshelwood mechanism).
6. Surface recombination of free charge carriers and surface exciton decay (step 9') occurs and is probably accompanied by luminescence.

5.4 Challenges in heterogeneous photocatalysis

There are three main challenges in the heterogeneous photochemistry shown in Fig. 5.24 that need to be considered if we are to understand the factors governing photochemical processes in heterogeneous systems. In some instances, one may wish to maximise photocatalytic activity, and in others to shut it down. Accordingly, factors that determine and influence the activity of photocatalysts need to be identified. The second, no less significant, challenge is to discover how one can manipulate the selectivity of photocatalysts, and what factors dictate this selectivity. For example, in such applications of photocatalysis as water and air purification, the goal is to achieve 100% mineralisation of the organic pollutants without also producing hazardous by-products. Of greater importance in heterogeneous photocatalysis, however, may be the photochemical synthesis of desired high-value chemicals. The last challenge remains how to improve the spectral sensitivity of solid metal-oxide photocatalysts so that they will absorb more light energy and thus significantly improve process efficiencies.

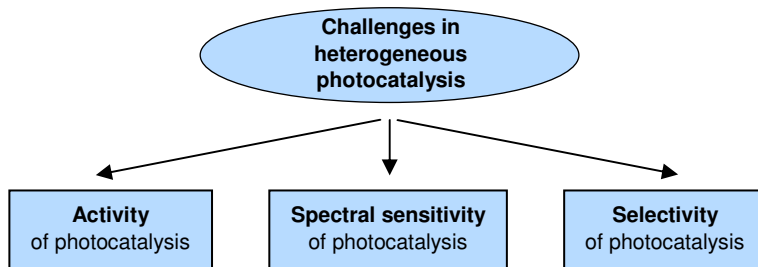


Figure 5.24 Challenges in photocatalysis..

5.4.1 Activity of a photocatalyst (photonic efficiency, quantum yield)

Of all the metal oxides, TiO_2 has been explored the most extensively as a means to ameliorate and detoxify polluted waters, air and soils by heterogeneous photocatalysis (Schiavello, 1987; Serpone and Pelizzetti, 1989; Pelizzetti and Schiavello, 1991; Ollis and Al-Ekabi, 1993; Rose *et al.*, 1994). The focus of most researchers in this area (notably the groups of Fujishima and Anpo in Japan) has been to develop highly photoactive TiO_2 specimens (Fujishima *et al.*, 2000; Watanabe *et al.*, 2000; Ohko *et al.*, 2001; Dohshi *et al.*, 2003; Takeuchi *et al.*, 2003a, 2003b). In spite of the large and excellent body of literature that demonstrates the utility of TiO_2 in such endeavours, understanding of the (primary) events in photocatalysis has lagged behind. For many years (Arana *et al.*, 2002; Lee *et al.*, 2003; Rao *et al.*, 2003), a major issue was the lack of an appropriate protocol to compare the activities of different photocatalysts in different heterogeneous systems. The quantitative description and characterisation of photoinduced processes in such heterogeneous systems remains a matter of current interest. In this regard, a protocol for measuring quantum yields of heterogeneous photocatalytic processes was reported by the group of Serpone (Serpone, 1997; Serpone and Salinaro, 1999; Salinaro *et al.*, 1999).

Knowledge of the quantum yield of a given event (*i.e.* the number of defined events which occur per photon absorbed by the system or as the quantity (mol) of reactant consumed or product formed per mol or Einstein of photons absorbed: see Kisch, 1989) has been central to homogeneous photochemistry. Photochemists have routinely determined quantum yields of reactant disappearance, product formation, light emission, and of other events occurring in a photochemical process.

In heterogeneous photocatalysis, *quantum yield* has for many years been taken to describe the number of molecules converted relative to the total number of photons

incident on the reactor walls for some undefined reactor geometry and for polychromatic radiation. In fact, as in homogeneous photochemistry, the quantum yield, ϕ_λ , should properly express the ratio of the moles of reactant consumed or product formed in the bulk phase, n , to the number (*i.e.* mol or Einstein) of photons at wavelength λ absorbed by the photocatalyst, n_{ph} , (eqs. 5.83). That is,

$$\phi_\lambda = \frac{n}{n_{\text{ph}}} \quad (5.83)$$

Methods to determine n_{ph} have been reported (Augugliaro *et al.*, 1991; Schiavello *et al.*, 1991; Palmisano *et al.*, 1993; Cabrera *et al.*, 1994). Alternatively, the quantum yield can be defined using the initial rate of reaction of the event, R^{in} , and the rate of photons *impinging on* and *absorbed by* the reaction system, as is common practice in homogeneous photochemistry. Thus

$$\phi_\lambda = \frac{R^{\text{in}}}{\rho_{0,\lambda}} \quad (5.84)$$

where $\rho_{0,\lambda}$ is the photon flow at wavelength λ . Analogous descriptions have been proposed for heterogeneous systems (Pichat, 1985; Braun *et al.*, 1991; Bahnemann *et al.*, 1991). In such systems, the relationships in eqs. 5.83 and 5.84 have been extended, modified and applied in an analogous fashion (Wubbels, 1983; Mirbach, 1984; Moggi *et al.*, 1984; Hennig *et al.*, 1985; Augugliaro *et al.*, 1991; Schiavello *et al.*, 1991; Palmisano *et al.*, 1993). However, owing to reflection, scattering, transmission (for transparent colloidal sols) and absorption by the suspended particulates, use of the term *quantum yield* referenced to *incident* photons in heterogeneous photocatalysis has only engendered confusion. To increase the confusion, some workers have used such terms as *apparent* and *true* quantum yields.

Since the numerator in eq. 5.84 expresses the rate of reaction, ϕ_λ will depend on the reactant concentration. As correctly noted by Braun and co-workers (1991) and emphasised by Cabrera *et al.* (1994), only for a zero-order reaction is ϕ_λ uniquely defined at the given wavelength λ because when the reaction rate depends on the reactant concentration, ϕ_λ falls off over time. In homogeneous photochemistry, this problem is normally overcome by determining ϕ_λ at small (less than ~10%) conversions of reactants, a point not often respected in heterogeneous photocatalysis, where the focus is often on complete mineralisation (100% transformation) of the substrate, at least in studies of environmental interest that focus on the total elimination of organic pollutants in water.

Additional considerations suggest that the photochemically defined *quantum yield* would be difficult to describe experimentally in heterogeneous media (Cabrera *et al.*,

1994), particularly for complex reactor geometries. Consequently, so-called quantum yields thus far reported in the literature have been the so-called 'apparent' or *lower limits* of the actual quantum yield, since scattered light was never accounted for (Pichat, 1985). In defining eqs. 5.83 and 5.84, it must also be recognised that photo-oxidations take place on the surface of the solid catalyst, and thus the catalytic properties of the catalyst surface may be important as the course of reactions is highly dependent on the characteristics of the surface on light activation. This called attention to the necessity of reporting the characteristics of the photocatalyst (Pichat, 1985; Palmisano *et al.*, 1993).

Widely ranging apparent quantum yields (*i.e.* photonic efficiencies, ξ ; see eq. 5.85 below) have been reported for the photodegradation of cresols and dimethylphenols. These ranged from 0.0076 to 0.010 and from 0.0060 to 0.015, respectively (2 g L⁻¹ TiO₂ and 20 g L⁻¹ of RH; Terzian, 1993). For the photodegradation of phenol, $\xi = 0.006$ (100 μ M phenol and 1 g L⁻¹ of TiO₂; Matthews and McEvoy, 1992), whereas for the photodegradation of 4-chlorophenol, $\xi = 0.015$ (8 g L⁻¹ TiO₂ and wavelength of irradiation was > 320 nm; Lepore *et al.*, 1993). For the case of H₂ formation from the reduction of water, ξ was 0.01 (Bahmenann *et al.*, 1984), and $\xi = 0.0012$ for the hydrogenolysis of methylacetylene CH₃C $\equiv$ CH (Anpo *et al.*, 1987). These reported apparent quantum yields often lacked information on the experimental conditions in which they were determined. It became clear that the quantum yield, as defined in homogeneous photochemistry, needed to be determined for such complex heterogeneous systems.

The numerator in eq. 5.84 is the rate of a catalysed heterogeneous reaction. This is related to the number of catalytically surface-active sites (Childs and Ollis, 1980). Unfortunately, until recently (Emeline *et al.*, 2005a) the number of such active sites has not been experimentally attainable (Serpone *et al.*, 1993a). To bypass this difficulty, the number of active sites has often been replaced (Boudart and Djega-Mariadassou, 1984) by (i) the surface area of the catalyst, or (ii) the mass of the catalyst, or (iii) the number of surface OH⁻ groups on a metal-oxide photocatalyst (Augugliaro *et al.*, 1991; Schiavello *et al.*, 1991; Palmisano *et al.*, 1993). None of these quantities, however, describes the actual heterogeneous rate since the measured surface area for a somewhat porous catalyst (for example) includes both external and internal surfaces (Basov *et al.*, 1977; Kurganov and Artem'ev, 1988; Emeline and Ryabchuk, 1997), and the internal surface may not be useful in some catalytic events. Also, not all the surface sites occupied by OH⁻ groups are necessarily catalytically active (Serpone *et al.*, 1993a), and depending on the reactor geometry, particle aggregation and stirring, not all the catalyst surface may be accessible to the substrate being photoconverted.

To overcome the necessity of having to stipulate reactor geometry and light source, together with the properties (*e.g.* size, surface area) of the photocatalyst material used, Serpone *et al.* (1993b, 1996) defined an efficiency that could be used to compare experiments within the same laboratory, and more importantly with other laboratories, in a way that would be reactor-independent. The proposed parameter was the *relative photonic efficiency*, symbolised as ξ_{rel} . This is related to an acceptable standard process, a standard photocatalyst material, and a standard ‘secondary actinometer’ in photocatalysed processes (Serpone *et al.*, 1996). In the experimental description of *relative photonic efficiency*, reactor geometry, light source and photocatalyst properties remained constant in assessing ξ_{rel} (Serpone *et al.*, 1993b). Also, when the appropriate quantum yield is experimentally unattainable, the term relative photonic efficiency avoids the unnecessary confusion with the terminology appropriately defined in homogeneous photochemistry (however, see Serpone and Salinaro, 1999; Salinaro *et al.*, 1999). Moreover, ξ_{rel} can be applied to whatever heterogeneous medium used: (i) dispersions, (ii) cases where the photocatalyst is immobilised on a support, and (iii) for solid/gas and solid/solution media.

In a practical application involving the photodegradation of phenolic substances, relative process efficiencies were obtained by relating the *initial rate* of substrate degradation, $R_{\text{substrate}}^{\text{in}}$ to the *initial rate of phenol degradation*, $R_{\text{phenol}}^{\text{in}}$, for constant incident photon flow $\rho_{\text{o},\lambda}$ reaching the reactor (note that the same reactor and reactor geometry must be used for both the substrate and phenol). Hence

$$\xi_{\text{rel}} = \frac{\frac{R_{\text{substrate}}^{\text{in}}}{\rho_{\text{o},\lambda}} \frac{\text{mol time}^{-1}}{\text{einstein time}^{-1}}}{\frac{R_{\text{phenol}}^{\text{in}}}{\rho_{\text{o},\lambda}} \frac{\text{mol time}^{-1}}{\text{einstein time}^{-1}}} \quad (5.85)$$

or simply

$$\xi_{\text{rel}} = \frac{R_{\text{substrate}}^{\text{in}}}{R_{\text{phenol}}^{\text{in}}} \quad (\text{dimensionless}) \quad (5.86)$$

where both (initial, hence zero-order) rates are obtained under otherwise identical conditions. To be useful, ξ_{rel} values must not depend on light irradiance and reactor geometry, or on such other parameters as pH, photocatalyst loading, substrate concentration and temperature.

With some caveats apparent later, another parameter that may characterise the photocatalytic activity of a heterogeneous system is the *photonic efficiency* (ξ , eq. 5.87; Serpone *et al.*, 1993b), which expresses the ratio of the rate of molecules

formed or degraded in the system, dN_r/dt (molecules s^{-1}) to the rate of *incident* photons impinging on the system, $dN_{hv(inc)}/dt$ (photons s^{-1}) at some given wavelength.

$$\xi = \frac{\frac{dN_r}{dt}}{\frac{dN_{hv(inc)}}{dt}} \quad (5.87)$$

In other words, photonic efficiency is a reaction rate normalised to the photon flow emitted by the light source. It describes how many molecules are transformed per photon incident on the system. Of course a more appropriate parameter to characterise the photochemical activity of heterogeneous systems is the more fundamental quantum yield (ϕ ; eq. 5.88) of the photoreaction, which expresses (Serpone and Emeline, 2002) the ratio between the rate of molecules formed or degraded in the system, dN_r/dt (molecules s^{-1}), and the rate of photons *absorbed* by the system, $dN_{hv(abs)}/dt$ (photons s^{-1}) at a given wavelength.

$$\phi = \frac{\frac{dN_r}{dt}}{A \left(\frac{dN_{hv(inc)}}{dt} \right)} = \frac{\frac{dN_r}{dt}}{\frac{dN_{hv(abs)}}{dt}} \quad (5.88)$$

In eq. 5.88, A is the absorbance (*i.e.* the fraction of the photon flow absorbed by the heterogeneous system). Thus, ϕ represents how many molecules are transformed per photon *actually absorbed*. The use of the term photonic efficiency in lieu of ‘quantum yields’ was proposed only to avoid confusion in terminology between heterogeneous photocatalysis and homogeneous photochemistry (Serpone *et al.*, 1993b, 1996). This parameter has also proved useful in describing the method to determine quantum yields through the limiting photonic efficiency approach (Serpone and Salinaro, 1999; Salinaro *et al.*, 1999) that will be described in detail below.

The essential difference between photonic efficiency ξ and quantum yield ϕ is that not every incident photon will necessarily act on the system and initiate chemical transformation. Thus ϕ may reach high values although ξ may be close to zero, especially when light is weakly absorbed. Difficulties in determining the fraction of absorbed light in heterogeneous systems have made the measurement of quantum yields difficult. This problem was solved in solid/gas heterogeneous systems by using diffuse reflectance spectroscopy with a standard reference sample, and a blackbody-like reactor. The standard experimental protocol for determining the fraction of absorbed light in solid/liquid heterogeneous systems employs an integrating sphere (Sun and Bolton, 1995; Serpone, 1997; Grela and Colussi, 1999).

To establish both the photonic efficiency and the quantum yield of a photo-stimulated reaction in heterogeneous systems, two important conditions (Emeline *et al.*, 1998a, 2000c), which unfortunately many researchers fail to consider, must be satisfied: (i) the reaction rate must scale linearly with photon flow ρ , and (ii) the reaction rate must be independent of the concentration $[M]$ of reagent molecules. Otherwise, where both photonic efficiency and quantum yield depend on photon flow and reagent concentration, the photocatalytic activities described by ξ and ϕ from different heterogeneous systems and different laboratories cannot be compared.

When the reaction rate of a photocatalytic process is given by eq. 5.89, the quantum yield of the process is given by eq. 5.90.

$$\left(-\frac{d[M]}{dt} \right)_{\rho, [M]} = (\text{const})[M]^n \rho^m \quad (5.89)$$

$$\phi = \frac{\left(-\frac{d[M]}{dt} \right)_{\rho, [M]}}{A \rho} = (\text{const})[M]^n \rho^{(m-1)} \quad (5.90)$$

Clearly, the quantum yield is a constant only if $n = 0$ and $m = 1$. Work by Emeline *et al.* (1998a, 2000c) has established that the reaction orders m and n can be interdependent. That is, the reaction order m varies with reagent concentration $[M]$ and the order n depends on photon flow ρ . For example, for the photodegradation of phenol over TiO_2 and the photostimulated adsorption of oxygen on ZrO_2 , $m \rightarrow 1$ if $n \rightarrow 0$, whereas $n \rightarrow 1$ if $m \rightarrow 0$. Results of kinetic studies (see Fig. 5.17) of both photostimulated processes have shown that the interdependence of the reaction rate can be generalised by eq. 5.91, which is identical with eq. 5.65.

$$\left(-\frac{d[M]}{dt} \right)_{\rho, [M]} = \frac{\alpha \rho [M]}{\beta \rho + \gamma [M]} \quad (5.91)$$

where the coefficients α , β , and γ are independent of photon flow and reagent concentration. Consequently, the quantum yield of a photochemical process can also be expressed by eq. 5.92, which shows that the necessary condition to determine the highest value of ϕ independent of concentration and light intensity is $\gamma[M] \gg \beta\rho$. Under such conditions, higher efficiencies of the photocatalyst at lower concentrations of reagent can be achieved at lower light intensities.

$$\phi_{(\rho, [M])} = \frac{\alpha [M]}{A(\beta \rho + \gamma [M])} \quad (5.92)$$

We have seen that the relative photonic efficiency (ξ_{rel}) introduced earlier (Serpone *et al.*, 1996) can compare photochemical activities of different heterogeneous systems. It can also be represented as the ratio between the photonic efficiency of a given reaction (ξ') to the photonic efficiency ξ_{st} of a standard reaction (the photodegradation of phenol and TiO₂ Degussa (now Evonik) P-25 were chosen for simplicity to describe the standard process and photocatalyst, respectively): see eq. 5.93.

$$\xi_{\text{rel}} = \xi' / \xi_{\text{st}} \quad (5.93)$$

Hence ξ_{rel} also equals the ratio of the corresponding reaction rates under otherwise identical irradiation conditions (eq. 5.94); see also eq. 5.86.

$$\xi_{\text{rel}} = \frac{\frac{dN'_r}{dt}}{\frac{dN_{r,\text{st}}}{dt}} \quad (5.94)$$

The relative photonic efficiency can also be expressed as the ratio of the appropriate quantum yields of the corresponding processes (eq. 5.95).

$$\xi_{\text{rel}} = \phi' / \phi_{\text{st}} \quad (5.95)$$

Using this approach and the quantum yield of the photodegradation of phenol over TiO₂ P-25, it was possible to estimate the corresponding quantum yields of photodegradation of other compounds through eq. 5.96 (Serpone and Salinaro, 1999).

$$\phi' = \xi_{\text{rel}} \phi_{\text{st}} \quad (5.96)$$

Thus, relative photonic efficiencies permitted for the first time the establishment of a correlation of the efficiency of a given process with similar work from other laboratories in the complex and active area of heterogeneous catalysis. The procedure for measuring ξ_{rel} is relatively simple and requires no sophisticated instrumentation.

On the basis of the above considerations, we now describe briefly the protocol(s) to assess the efficiencies of the photocatalytic process(es) (Salinaro *et al.*, 1999; Serpone and Salinaro, 1999). It will be necessary first to determine the photonic efficiency ξ of the heterogeneous process as expressed by eq. 5.87, remembering that the absolute values of ξ have little meaning since they are obtained for photons incident on, and not absorbed by, the reacting system. Nonetheless, they do provide a point of departure.

- Determine the photon flow $\rho_{o,\lambda}$ for the light source by regular actinometry using appropriate actinometric substances and the protocols described in the literature by Calvert and Pitts (1966) and Braun *et al.* (1991).
- Determine the initial rates R^{in} of photoconversion of the organic substrate RH for a range of concentrations of RH and for constant loading of the photocatalyst (for Degussa P-25 TiO_2 the initial loading was suggested to be 2 g L^{-1}).
- From the plot of R^{in} vs. $[\text{RH}]$ for constant TiO_2 loading and for constant light irradiance, determine the concentration range of RH that defines the plateau of the relationship $R^{\text{in}} = a[\text{RH}]/(1 + b[\text{RH}])$, where a and b are constants. Our experience with aromatic substrates suggests 20 mg L^{-1} may fall in this range. However, this may change depending on the nature of the substrate because of the connectivity between the irradiance of the light source used and the dependence of R^{in} on the concentration of substrate, as noted for both solid/gas and solid/liquid systems (Emeline *et al.*, 1998a).
- Choose a concentration of RH in this plateau, then determine the range of the photocatalyst TiO_2 loading which also defines the plateau of the plot of R^{in} vs. $[\text{TiO}_2]$, of the relationship $R^{\text{in}} = c[\text{TiO}_2]/(1 + d[\text{TiO}_2])$, where c and d are constants, to check that the TiO_2 loading suggested above at 2 g L^{-1} does indeed fall in the range.
- Photonic efficiencies ξ can then be estimated employing the relationship analogous to eq. 5.87, namely $\xi = R^{\text{in}}/\rho_{o,\lambda}$ at a given wavelength λ , for which not all the photons incident on the reacting system will be absorbed because of scattering and other similar effects.

Once the photonic efficiency for a given substrate has been estimated, and an analogous photonic efficiency for phenol has been determined under identical experimental conditions of reactor geometry, light irradiance from the same light source, and the same batch of photocatalyst material, then the relative photonic efficiency can be calculated. Relative photonic efficiencies have been reported for several aromatic substrates by Serpone and co-workers (1996). The recommended protocol to determine ξ_{rel} follows the steps below:

- Determine the initial rate of disappearance (or loss, or conversion) of phenol, $R^{\text{in}}_{\text{phenol}}$, in mol min^{-1} (note this is a zero-order process).
- Determine the initial rate of disappearance (or loss, or conversion) of the substrate RH being examined, $R^{\text{in}}_{\text{substrate}}$, also in mol min^{-1} and obtained under otherwise exact identical conditions as the initial rate for phenol.

- The relative photonic efficiency is calculated from eq. 5.93, in which ξ^* is the photonic efficiency of the substrate, which is given by $R_{\text{substrate}}^{\text{in}}/\rho_{\text{o},\lambda}$ and ξ_{st} is the photonic efficiency for phenol, given by $R_{\text{phenol}}^{\text{in}}/\rho_{\text{o},\lambda}$.

Equation 5.96 shows that the quantum yield for the photodegradation of a substrate is given by the product of the relative photonic efficiency of the substrate and the quantum yield for the disappearance of phenol. Accordingly, if the quantum yield of phenol degradation is known at a given wavelength (*e.g.* at 365 nm), then the quantum yields of various processes can be determined from the relative photonic efficiencies. This requires no sophisticated procedures as long as the same light source is used and experiments are carried out at the same time for the substrate and for the phenol standard on UV irradiation of the TiO₂ dispersion at 365 nm.

Following the method suggested by Sun and Bolton (1995) to determine the absorbance, *i.e.* the fraction of light actually absorbed by a substrate in a heterogeneous medium using diffuse reflectance spectroscopy, the quantum yield of phenol degradation was ascertained to be 0.14 ± 0.02 (see Table 5.3). This method is rather complex and requires instrumentation that is not often available in catalysis laboratories. A simpler method involves the photonic efficiencies, specifically the limiting photonic efficiency, of a process. This limiting photonic efficiency (eq. 5.97), obtained from plots of ξ vs. concentration of photocatalyst [Cat], is useful in that it provides a means to estimate quantum yields in a complex medium.

$$\xi = \frac{\xi_{\text{lim}} Q[\text{Cat}]}{(\xi_{\text{lim}} + Q[\text{Cat}])} = \frac{R^{\text{in}}}{\rho_{\text{o},\lambda}} \quad (5.97)$$

Table 5.3 Initial rates (R^{in}), photon flow at 365 nm (ρ_{o}), fraction of light absorbed at 365 nm (absorbance A) and quantum yields (ϕ_{dis}) for the photocatalysed oxidative conversion of phenol at ambient temperature and in air-equilibrated aqueous TiO₂ dispersions. Adapted from Salinaro *et al.* (1999).

TiO ₂ loading (g L ⁻¹)	10 ⁸ R^{in} (mol min ⁻¹)	10 ⁶ $\rho_{\text{o},365 \text{ nm}}$ (Einstein min ⁻¹)	$A_{365 \text{ nm}}$	$\phi_{\text{dis}}(\text{PhOH})$
0.060	0.54	2.13	0.0216	0.118
0.10	1.31	2.60	0.0359	0.140
0.15	1.91	2.13	0.0539	0.167
0.30	3.14	2.13	0.108	0.137
0.50	5.00	2.13	0.180	0.131
				$\phi_{\text{av.}} = \mathbf{0.14 \pm 0.02}$

Taking up the photonic efficiency in the form of eq. 5.97, for the case where $Q[\text{Cat}] \gg \xi_{\text{lim}}$ (here Q is a constant), *i.e.* for high loading in photocatalyst Cat, one obtains $\xi = \xi_{\text{lim}} = R^{\text{in}}/\rho_{0,\lambda}$, which is precisely the definition of the quantum yield ϕ (see eq. 5.84) if all the photons impinging on the reactor system are absorbed by the photocatalyst under high loading conditions. Under these conditions, the limiting photonic efficiency for irradiation at a given wavelength λ is the quantum yield of the process at the same wavelength; that is $\xi_{\text{lim}} = \phi_{\lambda}$. Note that if the initial rate data, R^{in} , were obtained under broadband (polychromatic) radiation in the wavelength range λ_1 to λ_2 , and if the integrated photon flow were determined in the same wavelength range, then the limiting photonic efficiency would be equivalent to the quantum yield ϕ_{poly} ; that is $\xi_{\text{lim}} = \phi_{\text{poly}}$.

For the case where Cat is TiO_2 , eq. 5.97 can be rewritten as the linear transform eq. 5.98, from which ξ_{lim} can be obtained from the intercept of the plot of ξ^{-1} vs. $[\text{TiO}_2]^{-1}$ illustrated in Fig. 5.25.

$$\frac{1}{\xi} = \frac{1}{\xi_{\text{lim}}} = \frac{1}{Q[\text{TiO}_2]} \quad (5.98)$$

The following steps summarise the protocol to obtain the quantum yield by the method of photonic efficiencies.

- Determine the photonic efficiency as indicated above for various photocatalyst loadings at a given wavelength. It is recommended that several data points be obtained at the lowest loadings possible in the $[\text{TiO}_2]$ range from 0.05 g L^{-1} to 1 g L^{-1} with as much precision as possible in each data point; subsequently, obtain data at loadings greater than 1 g L^{-1} to describe a complete curve as per eq. 5.97.
- Plot the linear transform ξ^{-1} vs $[\text{TiO}_2]^{-1}$ (eq. 5.98) illustrated in Fig. 5.25 for the photodegradation of phenol. From the intercept, the quantum yield of phenol degradation can be estimated as $\xi_{\text{lim}} = \phi_{\text{phenol}} \approx 0.12$, in fair agreement with the more laborious method described earlier, which gave a quantum yield for the disappearance of phenol to be $\phi_{\text{phenol}} = 0.14$.

The above procedure has been further tested by determining the quantum yield of the disappearance of 4-chlorophenol (4-CP) by the method of photonic efficiencies; the result was $\xi_{\text{lim}} = \phi_{4\text{-CP}} = 0.19 \pm 0.02$, in good agreement with the method of relative photonic efficiencies (eq. 5.95), which gave $\phi_{4\text{-CP}} = 0.17 \pm 0.02$ based on phenol as a sort of secondary actinometer.

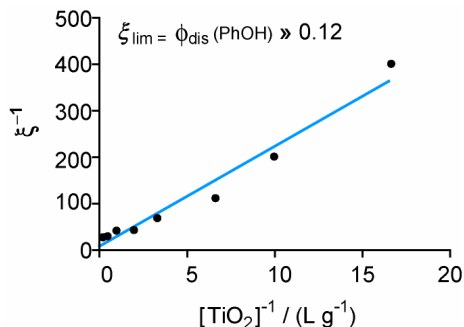


Figure 5.25 Double reciprocal plot of ξ^{-1} vs. $[\text{TiO}_2]^{-1}$ for the photodegradative oxidation of phenol, illustrating the procedure for obtaining quantum yields from the limiting photonic efficiency.

5.4.2 Simple primary surface reactions

To gain a better understanding of those factors that determine the efficiency of heterogeneous photocatalytic processes, Emeline *et al.* (1999a) undertook a theoretical study that considered both bulk and surface processes in the photocatalyst, along with primary and secondary chemical surface reactions. For simple primary photooxidative surface chemical reactions, reactions 5.99–5.101 are worth emphasising again.



Reaction 5.99 describes the oxidation of surface hydroxyl groups on the surface of the metal-oxide photocatalyst being oxidised by surface photogenerated holes. The subsequent reaction is recombination of surface-trapped holes ($\bullet\text{OH}_s$) with free surface electrons, whereas reaction 5.101 indicates addition of the $\bullet\text{OH}$ radical onto the molecule M, leading to oxidation of M as the $\text{M}-\bullet\text{OH}$ adduct. In the steady-state approach for the concentration of surface $\bullet\text{OH}_s$ radicals and charge carriers, the reaction rate ($-\text{d}[\text{M}]/\text{d}t$) can be described by eq 5.102.

$$\left(-\frac{\text{d}[\text{M}]}{\text{d}t} \right)_{\rho, [\text{M}]} = \frac{k_{99}k_{101}[\text{h}_s^+][\text{OH}_s^-][\text{M}]}{k_{100}[\text{e}_s^-] + k_{101}[\text{M}]} \quad (5.102)$$

A similar result is obtained for the photoreduction reaction with participation of such electron surface-active centres as Ti^{3+} (reactions 5.103–5.105).



Reactions 5.101 and 5.105 represent the primary oxidative and reductive chemical events of the catalytic cycle, respectively, and reactions 5.99 and 5.103 show the generation of surface-active centres, whereas reactions 5.100 and 5.104 reflect the deactivation of such centres. Both generation and deactivation of surface-active centres constitute a significant pathway of surface recombination of free carriers.

To the extent that the surface concentrations of free carriers are proportional to the actinic light irradiance, reaction 5.102 is equivalent to the experimental dependence expressed by eq. 5.91 and demonstrates the interdependence of the reaction rate on light irradiance and concentration of reagent. Hence, the necessary condition $\gamma [\text{M}] \gg \beta\rho$ to observe the higher quantum yield of the photocatalytic process is satisfied when $k_{101}[\text{M}] \gg k_{100}[\text{e}^{-}_{\text{s}}]$, that is when the rate of chemical decay of the surface-active sites is much greater than the rate of their physical recombination process. At constant light irradiance, which provides constant surface concentrations of free charge carriers, both eq. 5.91 and eq. 5.102 can easily be transformed into a Langmuir–Hinshelwood (LH) equivalent equation, although strictly speaking the mechanism represented by reactions 5.99–5.101 corresponds to the Eley–Rideal (ER) mechanism. For the LH pathway, M in reaction 5.101 represents the pre-adsorbed molecules of reagent, whose concentration is given by

$$[\text{M}_{\text{ads}}] = \frac{K[\text{S}_{\text{o}}][\text{M}]}{1 + K[\text{M}]} \quad (5.106)$$

The reaction rate expression is then

$$\left(-\frac{\text{d}[\text{M}]}{\text{d}t} \right)_{\rho, [\text{M}]} = \frac{k_{99}k_{101}K[\text{h}^{+}_{\text{s}}][\text{OH}^{-}_{\text{s}}][\text{S}_{\text{o}}][\text{M}]}{k_{100}[\text{e}^{-}_{\text{s}}] + (k_{100}[\text{e}^{-}_{\text{s}}] + k_{101}[\text{S}_{\text{o}}])K[\text{M}]} \quad (5.107)$$

Equation 5.106 can also be transformed into the classic Langmuir–Hinshelwood equation at constant light irradiance (see *e.g.* eq. 5.91); it demonstrates the interdependence of the reaction rate on light irradiance and concentration of reagent. However, in spite of the similar behaviour of ER and LH kinetics, there is nevertheless a difference in the approximations of the so-called apparent Langmuir constant (K_{L}) in the two mechanistic models, eqs. 5.108 and 5.109 (Emeline *et al.*, 2000b). At very high photon flow (*i.e.* when $[\text{e}^{-}_{\text{s}}] \rightarrow \infty$) $K_{\text{L}} \rightarrow 0$ in the ER pathway, whereas $K_{\text{L}} \rightarrow K$ in the Langmuir–Hinshelwood mechanism.

$$K_L = \frac{k_{101}}{k_{100}[\text{e}^-_s]} \quad (\text{ER - mechanism}) \quad (5.108)$$

$$K_L = \frac{(k_{100}[\text{e}^-_s] + k_{101}[\text{S}_\text{o}])K}{k_{100}[\text{e}^-_s]} \quad (\text{LH - mechanism}) \quad (5.109)$$

At sufficiently high concentration of reagent M, when the chemical reaction dominates the physical pathway of the surface recombination of carriers, the reaction rate is equal to the rate of generation of surface-active centres (*e.g.* surface $\bullet\text{OH}$ radicals for oxidative processes and electron centres, and Ti^{3+} for reductive reactions) and is proportional to the surface concentration of free charge carriers of the corresponding sign. From reaction 5.102 we obtain

$$-\frac{d[\text{M}]}{dt} = k_{99}[\text{h}^+_s][\text{OH}^-_s] \quad (5.110)$$

5.4.3 Colour centres and the band model of semiconductors

The conventional band model defines semiconductors (Fig. 5.26) in terms of two bands: the valence band, typically composed of $2p$ orbitals of the oxide O^{2-} ions in a metal-oxide semiconductor photocatalyst, and the conduction band, typically made up of the valence d orbitals of the metal ions. These two bands are separated by a forbidden bandgap (E_g) within which there typically exist surface states (ss). The two bands consist of a very large number of closely spaced energy levels, and when the semiconductor is illuminated with light of energy greater than the bandgap energy to generate free charge carriers, these carriers are expected to thermalise rapidly to the lowest energy level of the conduction band (CB) for electrons and to the 'lowest energy level' of the valence band (VB) for holes. Moreover, conventional wisdom,

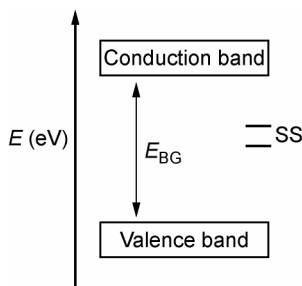
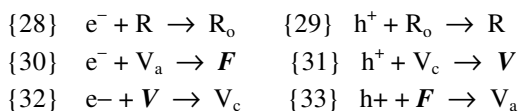


Figure 5.26 Conventional view of the band model of semiconductors; ss = surface states.

originating in large measure from photochemistry, dictates that whatever the ensuing redox reactions may be, they will take place from the lowest energy levels of a given charge carrier, so that there should be no spectral dependence of ϕ or any other parameter that assesses photon efficiencies.

After photoexcitation, generation of charge carriers occurs either from band-delocalised electronic states associated with the regular lattice (VB and CB), or from the intragap-localised electronic states associated with lattice irregularities or surface states (ss). The distinction between *intrinsic* (excitonic and band-to-band excitation) and *extrinsic* (excitation of impurities, defects and surface states) excitation is worth re-emphasising. Effects of surface absorption are also observed because of the peculiarity of surface processes (*e.g.* surface reconstruction and relaxation processes, and formation of new surface structures). *Extrinsic* absorption by solids normally occurs at lower energies than *intrinsic* absorption. Interestingly, *extrinsic* surface absorption can be red-shifted by as much as a few eV relative to the *intrinsic* fundamental absorption edge of wide-bandgap metal-oxide insulators.

The lifetime of photogenerated charge carriers is governed by a set of carrier recombination and trapping processes involving solid lattice defects, in particular anion and cation vacancies (V_a and V_c) and lattice ions in low-coordinated positions (see stages {28}–{33}):



Stages {28} and {29} describe fast electron–hole recombination through specific recombination centres R which generally determine the lifetime of carriers, whereas stages {30} and {31} represent carrier trapping by lattice defects such as V_a and V_c , to form the so-called *F*- and *V*-type colour centres with corresponding new absorption bands in the spectra of the solid. Stages {32} and {33} describe the decay of colour centres during irradiation by recombination with carriers of the appropriate sign. The latter process is typically slow enough to allow accumulation of photoinduced colour centres in solids. After irradiation is terminated, the lifetime of newly formed photoinduced colour centres can often be quite long.

Because of the exchange of charge carriers between the bulk and surface in a solid photocatalyst, there is a strong co-influence between surface processes (reactions 5.99–5.101 and 5.103–5.105) and bulk processes (stages {28}–{33}) involving free carriers, particularly between surface chemical reactions and photoinduced colouration of solids. Emeline *et al.* (1998a, 1998b) showed that the dominating

oxidative reaction leads to an increase in the formation of **F**-type electron colour centres, while domination of the reductive surface reaction causes the additional formation of **V**-type hole colour centres, as illustrated in Figs. 5.27 and 5.28 for ZrO_2 . The charge conservation law suggests that the relationship between the number of molecules taking part in the primary oxidative or reductive surface reactions and the number of colour centres of the corresponding type be represented by eq. 5.111.

$$\Delta[\mathbf{F}] + [\mathbf{M}^-] = \Delta[\mathbf{V}] + [\mathbf{M}^+] \quad (5.111)$$

where $\Delta[\mathbf{F}]$ and $\Delta[\mathbf{V}]$ are additional colour centres formed by surface reactions.

In addition to surface redox (external) processes, there is formation of defects and recombination events occurring in the bulk lattice that can also be considered as redox processes, albeit internal processes. For instance, formation of electron colour centres (*e.g.* Ti^{3+} in TiO_2 , Zr^{3+} in ZrO_2 , and **F**-type centres) is formally a reduction of lattice defect sites, whereas hole trapping by a lattice defect centre is formally an oxidative event (see *e.g.* eq. 5.72).

The decay of colour centres can also be caused by a photoionisation process resulting from photoexcitation of the solid in the corresponding absorption bands of photoinduced colour centres, reactions 5.112 and 5.113 (Ryabchuk and Burukina, 1991; Emeline *et al.* 1998b, 1999c).

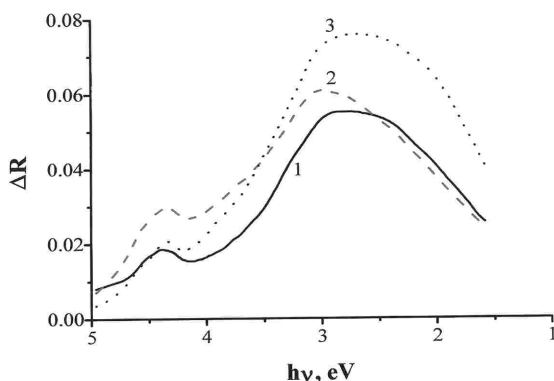


Figure 5.27 Difference diffuse reflectance spectra of powdered ZrO_2 irradiated with all UV/visible wavelengths for 45 min: (1) *in vacuo* { $\text{DRS}(\text{vac}) = R_o - R_{hv}(\text{vac})$ }; (2) in the presence of O_2 { $P = 100$ Pa; { $\text{DRS}(\text{O}_2) = R_o - R_{hv}(\text{O}_2)$ }; (3) in the presence of H_2 { $P = 100$ Pa; { $\text{DRS}(\text{H}_2) = R_o - R_{hv}(\text{H}_2)$ }. Reprinted in part with permission from Emeline *et al.* (1998b). Copyright (1998) American Chemical Society.

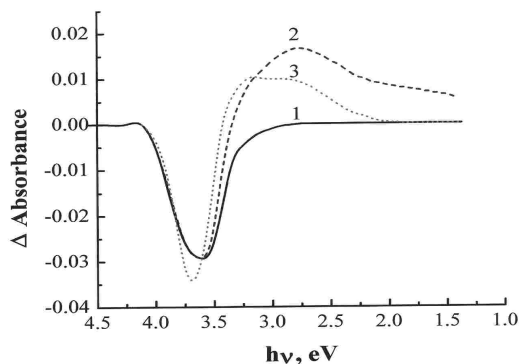


Figure 5.28 Difference absorption spectra of a non-irradiated original colloidal ZrO_2 sol and irradiated sol for 60 min at all the UV/visible wavelengths from the light source (spectrum 1), with methanol present (spectrum 2) and in the presence of oxygen (spectrum 3). Reprinted in part with permission from Emeline *et al.* (1998b). Copyright (1998) American Chemical Society.

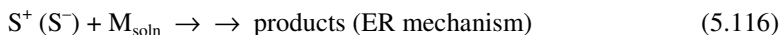
Such photoexcitation leads to the appearance of free charge carriers, which can participate in surface chemical reactions. Thus the spectral limit of surface photo-reactions becomes uncertain after irradiation is initiated, since the first colour centres are formed immediately and contribute to the absorption spectrum of the solid.

5.5 Theoretical description of quantum yields

5.5.1 Modelling

Absence of an electric field in the photocatalyst particle

To gain a theoretical insight into the factors that govern the activity of a metal-oxide photocatalyst, a very simple mechanism of the initial steps of a surface photochemical process is considered. It corresponds to the general mechanism of photoexcitation of the solid specimen (reactions 5.114–5.117) (see Figs. 5.12 and 5.23).



In eqs. 5.114–5.117, $S = \text{OH}^-_{(\text{S})}$ or $\text{Ti}^{4+}_{(\text{S})}$, $S^+ = \bullet\text{OH}_{(\text{S})}$, and $S^- = \text{Ti}^{3+}_{(\text{S})}$. Taking TiO_2 as exemplifying a metal-oxide particle, the mechanism involves three essential steps. The first is formation of surface-active centres (reaction 5.114) caused by trapping of a charge carrier by a surface defect, which in the case of TiO_2 may be a low-coordinated surface Ti^{4+} ion or a surface OH^- group. The second is the decay of active centres (reaction 5.115) due to recombination with charge carriers of the opposite sign. The third is the initial step of the chemical sequence (reactions 5.116 and 5.117), namely the interaction of a molecule of the reagent M with localised charge carriers, *i.e.* surface-active centres.

Application of the steady-state condition to the concentration of surface-active centres (eq. 5.118) and carriers (eqs. 5.119 and 5.120) gives a reaction rate that can be represented by reaction 5.121 for the surface reaction involving the substrate.

$$\frac{d[S^+]}{dt} = 0 \quad \text{and} \quad \frac{d[S^-]}{dt} = 0 \quad (5.118)$$

$$[e^-] = \alpha \rho \tau \quad (5.119)$$

$$[h^+] = \alpha \rho \tau_h \quad (5.120)$$

$$\text{Rate} = \frac{k_{114} k_{116} [S] \alpha \rho \tau_h [M]}{k_{115} \alpha \rho \tau_e + k_{116} [M]} \quad (5.121)$$

At high concentrations of M , $k_{116} [M] \gg k_{115} \alpha \rho \tau$, and the rate becomes

$$\text{Rate} = k_{114} [S] n \quad (5.122)$$

where n is the number of carriers and is equal to $\alpha \rho \tau$. This means that high substrate concentrations provide the conditions in which decay of the active centres through recombination is suppressed by the chemical step. The quantum yield therefore represents the efficiency of photogeneration of surface-active centres, given by

$$\phi = \frac{k_{114} [S] n_s}{A \rho} \quad (5.123)$$

The latter implies that under the above conditions the quantum yield depends on k , the concentration of surface-active centres $[S]$, and the surface concentration of charge carriers, n_s (A is the fraction of light absorbed, *i.e.* absorptance, and ρ is the photon flow). It is therefore possible to query those factors that govern the surface concentration of charge carriers, and the activity of the photocatalyst through the quantum yield ϕ . For this, the functionality of the surface charge-carrier concentration and the parameters that affect it need to be examined.

The surface concentration of free charge carriers can be determined from the solution to the continuity equation, eq. 5.124, under the steady-state approximation and with suitable boundary conditions, such as $J_s = s n_s$ (Emeline *et al.*, 2003),

$$\frac{\partial n(x,t)}{\partial t} = -\frac{\partial J_n(x,t)}{\partial x} - \frac{n(x,t)}{\tau} + G(x,t) = 0 \quad (5.124)$$

where $n(x,t)$ is the concentration of free charge carriers at a given point in space with spatial coordinates x at some time t ; $J(x,t)$ is the flow of charge carriers caused either by diffusion or by drift; $G(x,t)$ is a time-space function of carrier photogeneration; τ is the lifetime of carriers in the bulk of the solid; and s is a constant of the surface recombination events represented by reactions 5.99 and 5.100, and 5.103 and 5.104.

Surface recombination processes are similar to those in the bulk. However, surface defects such as corners, edges, terraces, dislocations and new near-surface structures) can lead to a greater rate of carrier recombination on the surface compared with the bulk, causing a decrease of the concentration $n(x)$ of carriers in the near-surface space in the solid. The decrease in $n(x)$ leads to diffusion of carriers $\{J_n\}$ from the bulk to the surface, as given by eq. 5.125.

$$\{J_n\} = -D \frac{\partial n}{\partial x} \quad (5.125)$$

Another cause for the flow of carriers to or from the surface is surface charge, which can cause carriers to drift in a direction determined by the charge of the carriers and the charge on the surface (eq. 5.126),

$$J_n = u n(x) \mathcal{E}(x) \quad (5.126)$$

where u is the mobility of the carriers, and $\mathcal{E}(x)$ is the electric field at a distance x from the surface. However, if the size of the photocatalyst particles is much less than the Debye screening length (*i.e.* the width of the space-charge layer), the contribution of carrier drift to carrier flow becomes negligible.

The solution of the continuity equation, eq. 5.124, for a one-dimensional plate model (Emeline *et al.*, 1999a) that takes into consideration a non-uniform function of carrier generation and obeys the Lambert–Beer law and has diffusion as the major path of carrier flow gives the spatial distribution of carriers in the bulk of the solid shown in Fig. 5.29. The expression for the surface carrier concentration n_s , which on substitution into eq. 5.110 for the reaction rate, followed by substitution of the resulting expression into eq. 5.88 for ϕ {where $A = 2(1 - e^{-ad})$ for the solid plate irradiated from both sides}, yields eq. 5.127 for the quantum yield ϕ of the primary surface chemical process (Emeline *et al.*, 1999a).

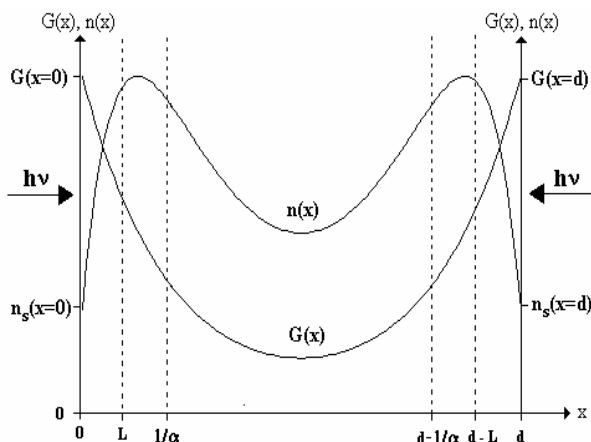


Figure 5.29 Scheme of a solid plate of thickness d irradiated uniformly from both sides. The curve $G(x)$ describes the non-uniform spatial distribution of carrier photogeneration. The straight vertical lines between the surface and the bulk define a depth equal to the average diffusion length of the carriers L and average length $1/\alpha$ of light penetration into the bulk. The carriers generated within the diffusion length can reach the plate surfaces by diffusion migration. Those generated in the remaining part of the lattice bulk cannot take part in surface chemical processes. The curve $n(x)$ represents the spatial distribution of the concentration of free charge carriers. Reprinted with permission from Emeline *et al.* (1999a). Copyright (1999) American Chemical Society.

$$\phi = \frac{k_{tr} [S] \chi \rho \alpha L^2}{D \left(\tanh\left(\frac{d}{2L}\right) + \zeta \right) (1 - \alpha^2 L^2)} \left[\tanh\left(\frac{d}{2L}\right) \coth\left(\frac{\alpha d}{2}\right) - \alpha L \right] \quad (5.127)$$

where α is the absorption coefficient, d is the thickness of the plate, $L = (D\tau)^{1/2}$ is the diffusion length of carriers, ζ is a ratio of rates of surface to bulk recombinations, $[S]$ is the concentration of surface-active sites (*e.g.* surface OH^- groups or surface electron traps, Ti^{4+} in TiO_2), χ is the internal quantum yield of photoeffects, and k_{tr} is the rate constant for trapping of charge carriers (either k_{114a} or k_{114b} of reactions 5.114a and 5.114b).

Equation 5.127 suggests that a spectral variation of the absorption coefficient α leads to a spectral variation of ϕ of the chemical process, and permits inferences as to the conditions that determine whether ϕ is spectrally dependent or independent. Specifically, ϕ becomes spectrally independent in the case of very strong fundamental absorption (*i.e.* when $\alpha \rightarrow \infty$), and when absorption is weak (*i.e.* for $\alpha \rightarrow 0$) corresponding to *extrinsic* light absorption. The quantum yield is also spectrally

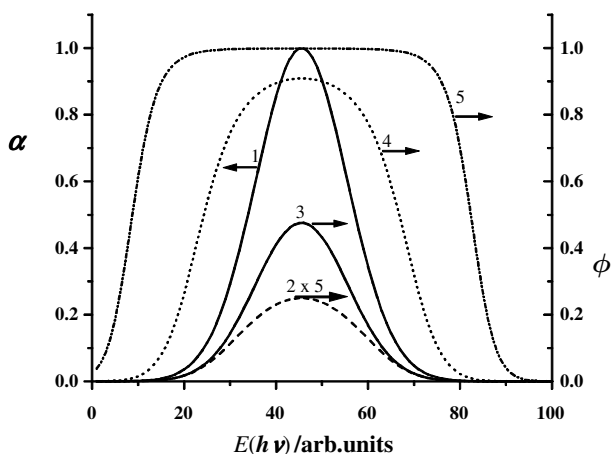


Figure 5.30 Spectral dependencies of the quantum yield within a single absorption band – curve 1 (note that α is in relative units); curves 2–5 for different values of the dimensionless factor αL : (curve 2), $\alpha L = 0.1$; (curve 3), $\alpha L = 1$; (curve 4), $\alpha L = 10$; (curve 5), $\alpha L = 1000$. Reprinted with permission from Emeline *et al.* (1999a). Copyright (1999) American Chemical Society.

independent in the case of light absorption by surface states. When αL is comparable to unity, ϕ becomes spectrally dependent and increases with increasing absorption coefficient α (see *e.g.* Fig. 5.30), because the spectral variations of α change the number of carriers generated within the diffusion length (L) from the surface that can reach the surface and participate in surface photoreactions. For weak light absorption, the ratio of the number of such carriers to the number of absorbed photons is a constant, and thus ϕ of a surface photoreaction on a given photocatalyst depends on the ratio $d/2L$ which, in the one-dimensional model, is proportional to the ratio between the total volume of the bulk crystal ($V_{\text{cryst.}} \propto d$) and the volume of the bulk space near the surface ($V_{\text{dif.}} \propto 2L$) from which photogenerated carriers can reach the surface by diffusion (Emeline *et al.*, 1999a). In other words, for a full three-dimensional particle model, ϕ depends on the ratio r/L , where r is the radius of the particle.

During the growth of the absorption coefficient α , more carriers are generated within the diffusion length distance from the surface, leading to an increase in ϕ of the surface chemical reactions. For the case of very strong absorption, all the charge carriers are generated within the diffusion length and with a certain probability of participating in surface processes.

Significant inferences can be drawn from the solution (eq. 5.127) to the continuity equation, eq. 5.124, for the quantum yields (Emeline *et al.*, 1999a):

- The quantum yield ϕ of the surface reaction depends on the ratio d/L .
- The smaller d/L is, the smaller is the fraction of carriers in the bulk that diffuse to the surface, and hence the greater is the fraction of absorbed photons that are inactive.
- The quantum yield decreases as the ratio d/L increases.
- The smaller the particle size d , the smaller is the ratio d/L , and the greater ϕ will be.
- *Most important*, the quantum yield ϕ increases as d decreases. That is, there is no need to invoke quantum size effects to explain increased quantum efficiencies of surface reactions with decreasing particle size, since an increase in ϕ with decreasing size of the particles is a natural consequence of the model.
- The greater the mobility of carriers is (thus the longer the diffusion length L), the greater is ϕ for a given crystal size d and absorption coefficient α .

Subsequent to the rather complex expression, eq. 5.127, for the quantum yield of a photoreaction that takes place on the surface of a (metal-oxide) photocatalyst, it must be recognised that complex events take place when the absorption spectra of solids are formed by the overlap of several single absorption bands belonging to different types of light absorption, and that differ either (a) by their abilities to form free carriers (internal quantum yield of photoeffects) and/or (b) by the properties (mobility, lifetime) of newly generated charge carriers. Experimentally, Emeline *et al.* (1999c, 2000a) have shown that the former cause (a) is often implicated in weak *extrinsic* light absorption by defects, which leads to band-like or step-like spectral dependencies of the quantum yields of processes occurring on metal oxides such as Sc_2O_3 (Fig. 5.31) and MgO (Fig. 5.32) whose shape is dictated by the degree of overlap of single absorption bands of different types (particularly by the degree of overlap of active and inactive light absorption), whereas the latter reason (b) becomes important in the spectral range of *intrinsic* (fundamental) light absorption by the solid where hot carriers generated at a photon energy greater than the bandgap energy can be involved in surface processes. In such a case, in addition to the spectral variations of ϕ caused by the spectral variation of the absorption coefficient α (see above), especially at the fundamental absorption edge, the spectral dependence of ϕ may also originate from the spectral variation of the mobilities and lifetimes of carriers generated at different wavelengths (see eq. 5.127).

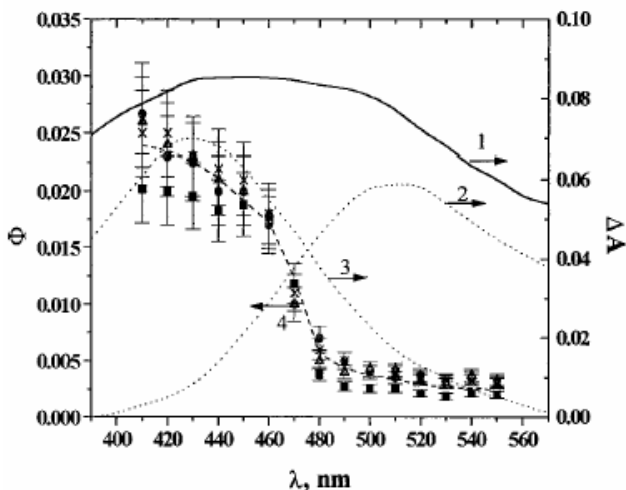


Figure 5.31 Spectral dependencies of quantum yields ϕ of photoadsorption of hydrogen ($\blacktriangle$), methane ($\times$) and carbon monoxide ($\bullet$) and photodesorption of pre-adsorbed oxygen ($\blacksquare$) on Sc_2O_3 within the spectral absorption region of photogenerated colour centres (curve 1). Spectra 2 and 3 demonstrate the overlap of the two active single Gaussian-shaped absorption bands in the given spectral region (see Fig. 5.27 below). The calculated spectral dependence of the quantum yields of surface photoprocesses in the given spectral region is presented by curve 4 (dashed line). Reprinted with permission from Emeline *et al.* (1999b). Copyright (1999) American Chemical Society.

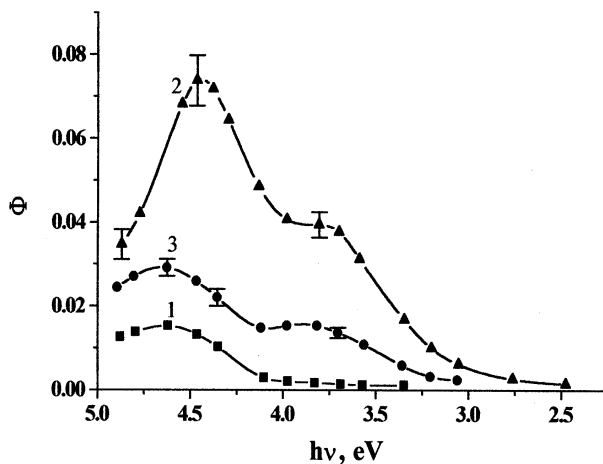


Figure 5.32 Spectral dependencies of quantum yields ϕ of photoadsorption of oxygen (1), hydrogen (2) and methane (3) on powdered MgO . Reprinted with permission from Emeline *et al.* (2000a). Copyright (2000) American Chemical Society.

This is because different direct and indirect band-to-band transitions lead to different initial populations of the electronic states in the bands. The latter factor is essential provided that communication between different energy levels within the bands is weak enough to render fast thermalisation of hot carriers unlikely. In this case, competition between diffusion of carriers toward the surface and their loss of energy are quite effective in small particles and promote the involvement of carriers with excess energy into surface processes. The latter may also affect the reactivity of surface-active sites. Experimental spectral dependencies of quantum yields (Emeline *et al.*, 2000a, 2000c) of several surface photochemical processes over TiO_2 (Figs. 5.33 and 5.34), both in the rutile and anatase forms, demonstrate a spectral band-like structure with maxima corresponding to the energies of indirect and direct electron transitions in TiO_2 .

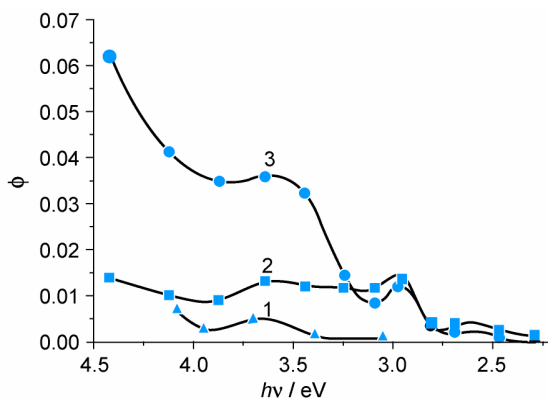


Figure 5.33 Spectral dependencies of quantum yields ϕ of photoadsorption of oxygen (at $T = 100$ K) (1), hydrogen (2), and methane (3) on powdered TiO_2 (rutile). Reprinted in part with permission from Emeline *et al.* (2000a). Copyright (2000) American Chemical Society.

The observations shown in Figs. 5.33 and 5.34 strongly indicated the need to re-examine the conventional model of semiconductors, which assumes continuity of carrier states within the valence and conduction bands. This model implies fast thermalisation of hot carriers and assumes that free carriers involved in surface processes have the same properties (lifetimes, mobilities and reactivities) regardless of the energy of excitation. It became obvious that there was a need to consider the possibility that different electronic transitions produced by photoexcitation at different wavelengths can lead to different distribution(s) of population of the photoactive electronic states (Fig. 5.35; Emeline *et al.*, 2000c) depending on which type of band-to-band transition (direct or indirect) dominated at those wavelengths.

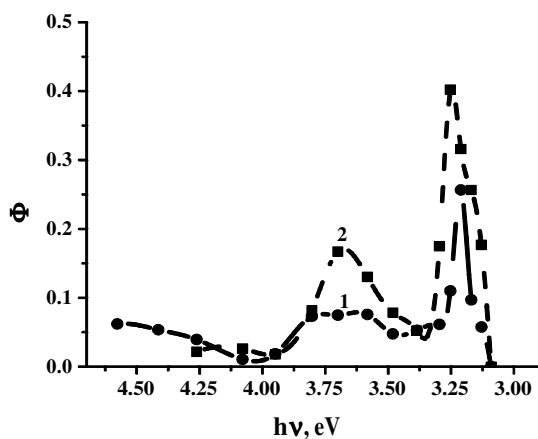


Figure 5.34 Spectral dependencies of the quantum yield ϕ of photodegradation of phenol (1) and 4-chlorophenol (2) over TiO_2 (P-25). Reprinted with permission from Emeline *et al.* (2000c). Copyright (2000) American Chemical Society.

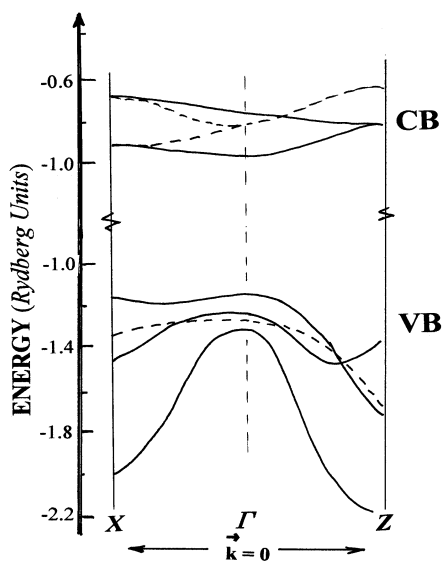


Figure 5.35 Graph illustrating the relevant valence-band (VB) and conduction-band (CB) states in the Brillouin zone for a TiO_2 crystal in the X and Z edges, and in the crystal centre Γ . Note that the lowest energy direct transition from the lowest energy of the valence band to the lowest level of the conduction band at Γ is forbidden; the lowest energy transition is an indirect phonon-assisted transition. Adapted with permission from Emeline *et al.* (2000c). Copyright (2000) American Chemical Society.

This could lead to different pathways for carrier relaxation in the momentum/energy space that is dictated by the distribution of probabilities of carrier thermalisation from the initial photoexcited states to the quasi-thermalised excited states of the carriers. Such distribution(s) depends on the degree to which the different levels occupied after photoexcitation at a given wavelength communicate with each other. Otherwise, it may lead to different energetic states of free carriers, and thus to the different kinetic behaviour of the carriers in terms of their lifetimes, mobilities, and rate constants for e^-/h^+ recombination through specific recombination centres. In other words, photocarriers generated at different photoexcitation wavelengths, corresponding to different electronic transitions, have a different probability of initiating surface chemical reactions, resulting in the spectral dependence of the quantum yield.

5.5.2 Presence of an electric field in the photocatalyst particle

In this section we examine the case where there is an electric field in photocatalyst particle and ask what influence such an electric field might have on the photocatalytic behaviour of the photocatalyst particles. Accordingly, we now modify the earlier model (Fig. 5.29) to include the electric field, whose presence may affect both the magnitude and the direction of migration of the photogenerated carriers. We then query what factors govern the surface concentration of carriers, and thus the quantum yield of the surface reaction under these new conditions.

Solution of the continuity equation, eq. 5.124 (Emeline *et al.*, 1999a), that assumed no electric field existed in the particle gave the concentration of surface charge carriers and consequently could define the functionality of the quantum yield ϕ (eq. 5.127). However, for particles greater than ~ 5 nm (diameter) the existence of an electric field $\mathcal{E}(x)$ cannot be neglected. The latter can give rise to drift of one charge carrier toward the particle surface and the other charge carrier away from the surface depending on the surface charge, as described by the surface potential U_s which can be either positive or negative. Accordingly we now consider the simplified one-dimensional model of Fig. 5.36 (Emeline *et al.*, 2003), which depicts the solid photocatalyst as a solid plate illuminated from both sides, and with both surfaces separated by the solid's bulk at a distance of $2d$. The surface potential U_s was allowed to decay linearly in the subsurface charge region (denoted here as δ) and becoming zero at point q . This means that the electric field is constant in the δ region and is zero in the middle region of the plate (from q to $-q$).

It was also assumed that the light irradiance I obeys exponential decay characteristics due to absorption of light by the solid photocatalyst. To describe the concentration of surface charge carriers for the above model, the continuity equation (eq. 5.124) was rewritten under steady-state conditions as expressed by eq. 5.128

$$-\frac{\partial j(x,t)}{\partial x} - \frac{n(x,t)}{\tau} = -g(x,t) \quad (5.128)$$

where

$$\frac{\partial n(x,t)}{\partial t} = 0 \quad (5.129)$$

and n is the concentration of charge carriers at depth x , j is the charge-carrier flow which originates from diffusion (j_{diff}) of the charge carriers and drift of the charge carriers (j_{drift}) in the presence of the electric field $\mathcal{E}(x)$ such that $j = j_{\text{drift}} + j_{\text{diff}}$. At the surface, the charge flow is consumed through surface recombination (s).

The model above clearly illustrates three space-charge regions in the plate, two of which (regions n_1 and n_3) are within a distance δ from the surface where both diffusion and drift of the charge carriers can occur, whereas the third region n_2 (from q to $-q$) is quasineutral. Here only diffusion of carriers can take place and this defines the charge current.

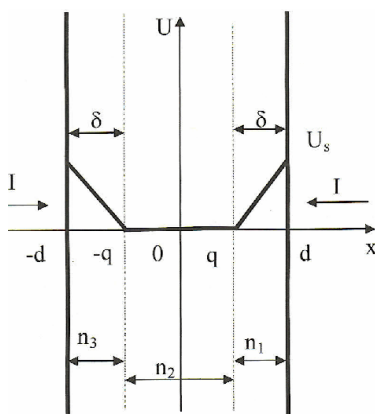


Figure 5.36 Model of a solid plate of photocatalyst of thickness $2d$ irradiated uniformly from both sides (I). The graph also defines the surface potential U_s , and the width of the near-surface space charge region δ . Reprinted with permission from Emeline *et al.* (2003). Copyright (2003) American Chemical Society.

If the rate of charge-carrier generation at a given point in the bulk is proportional to the light irradiance (I) at that point, and the irradiance obeys exponential decay kinetics, the spatial distribution $g(x)$ of photogeneration of charge carriers is given by

$$g(x) = \chi\alpha I e^{-\alpha d} (e^{\alpha x} + e^{-\alpha x}) = 2\chi\alpha I e^{-\alpha d} \cosh(\alpha x) \quad (5.130)$$

Determination of the quantum yield requires knowledge of the rate of absorption of photons given by expression 5.131.

$$\frac{dN_{hv}}{dt} = 2\alpha I (1 - e^{-2\alpha d}) \quad (5.131)$$

Application of suitable boundary conditions to the solution of the continuity equation for the charge-carrier concentration n_s and application of eq. 5.131 yields the very complex expression 5.132 for the quantum yield ϕ , which arises more from mathematics than from the physics of the problem (for a derivation and definition of some of the parameters used, see Emeline *et al.*, 2003).

$$\begin{aligned} \phi = & \frac{\chi\alpha k_t S \coth \alpha d}{D[\varepsilon^2 \alpha^2 - (\alpha^2 - \beta^2)^2]} \times \\ & \left\{ \frac{(\lambda_2 - \lambda_1)(\cosh \alpha d - \tanh \alpha d \sinh \alpha d) \left\{ \frac{\varepsilon^2 \alpha^2 - (\alpha^2 - \beta^2)^2}{\alpha^2 - \beta^2} [\alpha \tanh \alpha(d - \delta) - \beta \tanh \beta(d - \delta)] \right\}}{e^{-\lambda_1 \delta} (\lambda_1 - \frac{S}{D}) [\beta \tanh \beta(d - \delta) + \lambda_2] - e^{-\lambda_2 \delta} (\lambda_2 - \frac{S}{D}) [\beta \tanh \beta(d - \delta) + \lambda_1]} \right. \\ & + \frac{(\lambda_2 - \lambda_1)(\cosh \alpha d - \tanh \alpha d \sinh \alpha d) \{ [(\alpha^2 - \beta^2) - \varepsilon \alpha \tanh \alpha(d - \delta)] [\varepsilon - \beta \tanh \beta(d - \delta)] - \alpha [\varepsilon \alpha - (\alpha^2 - \beta^2) \tanh \alpha(d - \delta)] \}}{e^{-\lambda_1 \delta} (\lambda_1 - \frac{S}{D}) [\beta \tanh \beta(d - \delta) + \lambda_2] - e^{-\lambda_2 \delta} (\lambda_2 - \frac{S}{D}) [\beta \tanh \beta(d - \delta) + \lambda_1]} \\ & + \left. \frac{e^{-\lambda_1 \delta} [\beta \tanh \beta(d - \delta) + \lambda_2] [(\alpha^2 - \beta^2)(\lambda_2 - \alpha \tanh \alpha d) + \varepsilon \alpha (\alpha - \lambda_2 \tanh \alpha d)]}{e^{-\lambda_1 \delta} (\lambda_1 - \frac{S}{D}) [\beta \tanh \beta(d - \delta) + \lambda_2] - e^{-\lambda_2 \delta} (\lambda_2 - \frac{S}{D}) [\beta \tanh \beta(d - \delta) + \lambda_1]} \right. \\ & \left. - \frac{e^{-\lambda_2 \delta} [\beta \tanh \beta(d - \delta) + \lambda_1] [(\alpha^2 - \beta^2)(\lambda_1 - \alpha \tanh \alpha d) + \varepsilon \alpha (\alpha - \lambda_1 \tanh \alpha d)]}{e^{-\lambda_1 \delta} (\lambda_1 - \frac{S}{D}) [\beta \tanh \beta(d - \delta) + \lambda_2] - e^{-\lambda_2 \delta} (\lambda_2 - \frac{S}{D}) [\beta \tanh \beta(d - \delta) + \lambda_1]} \right\} \quad (5.132) \end{aligned}$$

In fact, eq. 5.132 can easily be understood and even simplified by considering particular cases. For instance, in the absence of the electric field, it simplifies to eq. 5.133, which is identical with the expression obtained earlier (eq. 5.127) with the model depicted in Fig. 5.29.⁵

⁵ Note that $\zeta = sL/D$ and the factor 2 is missing because the plate thickness in the model of Fig. 5.36 was defined somewhat differently (Emeline *et al.*, 2003) from the model displayed in Fig. 5.29.

$$\phi = \frac{\chi k_r [S] \alpha L^2}{D(1 - \alpha^2 L^2)} \times \frac{\tanh \frac{d}{L} \coth \alpha d - \alpha L}{\tanh \frac{d}{L} + \frac{sL}{D}} \quad (5.133)$$

In spite of the complexity of eq. 5.132, some physical features are worth noting:

- αL expresses the ratio between that part of the solid bulk where the photo-generation of charge carriers occurs and that part from which the carriers can reach the surface as a result of diffusion; if $\alpha L > 1$, all photogenerated charge carriers can diffuse to the surface.
- $\alpha \mathcal{E}$ defines the relationship between the bulk region where the photocarriers are generated and the region from which charge carriers migrate to the surface through diffusion and drift; if $\alpha \mathcal{E} > 1$, all photogenerated charge carriers of the appropriate sign can drift to the surface.
- $\alpha \delta$ is the correlation between the depth of light penetration into the bulk solid and the distance from the surface where the electric field is most significant.
- αd and $\alpha(d - \delta)$ reflect respectively the spatial non-uniformity of carrier photo-generation in the whole bulk of the solid and in that part of the bulk where only diffusion is the pathway for carrier migration.
- ε , β and $\lambda_{1,2}$ characterise the migration of carriers in the bulk and reflect the relationship between the efficiency of diffusion and drift migration of the carriers (see Emeline *et al.*, 2003 for details).
- $(\lambda_{1,2} - s/D)$ is proportional to the ratio between surface recombination and bulk recombination of charge carriers.

As is evident from the above physical correlations and the general solution for ϕ (eq. 5.132), key parameters/factors that determine the value of ϕ are the absorption coefficients α and the electric field $\mathcal{E}(x)$, which in the model of Fig. 5.36 depend on the value(s) of the surface potential U_s . This implies that the spectral variation of the absorption coefficient is a major cause of the spectral variation of ϕ .

Figure 5.37 shows the calculated dependencies of ϕ on the absorption coefficients α for the case of strong light absorption and for different values of the surface potential U_s . In all cases, ϕ increases with increasing α . This has a very simple physical meaning: the stronger the light absorption, the closer the photogeneration of carriers is to the surface, and therefore the greater is the number of carriers that can reach the surface and participate in surface chemical reactions. The maximal value of ϕ , observed at very high light absorption when practically all the charge carriers are able to reach the surface, is limited only by the rate of recombination s .

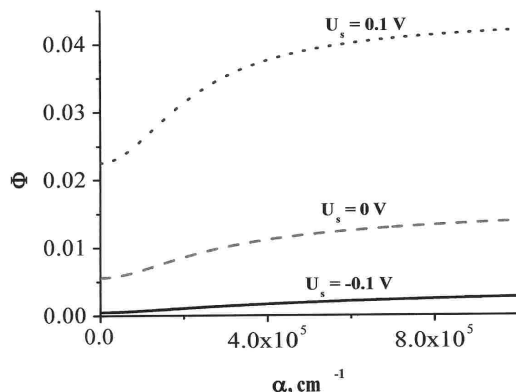


Figure 5.37 Theoretical dependencies of the quantum yield ϕ of a surface photochemical reaction involving electrons (for the case of strong light absorption) on the absorption coefficient at different surface potentials U_s . Note that the scale in ϕ is arbitrary—important is the trend in ϕ with increase in α . Reprinted with permission from Emeline *et al.* (2003). Copyright (2003) American Chemical Society.

For small values of α (weak absorption of light), ϕ remains constant (Fig. 5.38) (Emeline *et al.*, 2003). The physical sense of the term *weak absorption* is that the decay of the light intensity in the bulk is so weak that the light irradiance, and thus the volume rate of photogeneration of carriers, can be assumed to be the same at any point in the bulk of the plate. Accordingly, the fraction of carriers that can reach the surface through diffusion and/or drift is constant. Mathematically, this means that the depth of penetration of light ($1/\alpha$) is much greater than the thickness of the plate ($2d$). Consequently, for *weak light absorption* within a single absorption band, ϕ of the surface chemical reaction should be spectrally invariant, whereas for the case of *strong light absorption* ϕ should be spectrally variable (Fig. 5.37).

Figure 5.39 shows theoretical spectral dependencies of the quantum yield of photoinduced surface chemical reactions in a single absorption band for the case of *weak light absorption* (Emeline *et al.*, 2003) where the absorption coefficient α does not exceed $2 \times 10^3 \text{ cm}^{-1}$. The calculated ϕ are spectrally invariant, depending only on the value of the surface potential U_s . By comparison, Fig. 5.40 depicts the absorption band of photogenerated *F* colour centres in powdered KBr (Emeline *et al.*, 2000a) with $\alpha < 10^3 \text{ cm}^{-1}$ and crystallite size $< 10^{-4} \text{ cm}$, which satisfies the conditions for weak light absorption. Also illustrated in Fig. 5.40 are the quantum yields determined for the photostimulated adsorption of molecular oxygen on solid KBr during photoexcitation in the *F* band. Within experimental error, ϕ for the photoadsorption of oxygen is spectrally invariant (see curve 2; Fig. 5.40).

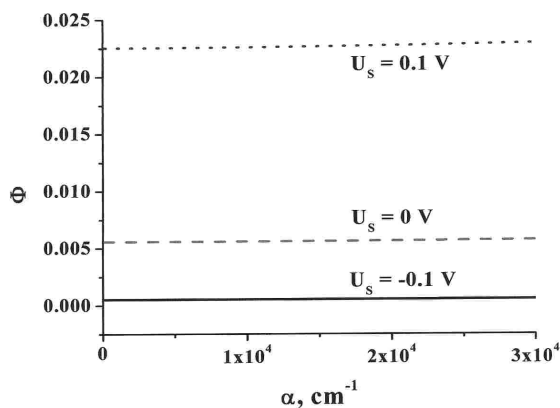


Figure 5.38 Theoretical dependencies of quantum yield ϕ of a surface photochemical reaction involving electrons on the absorption coefficient at different surface potentials U_s (case of weak light absorption). Reprinted with permission from Emeline *et al.* (2003). Copyright (2003) American Chemical Society.

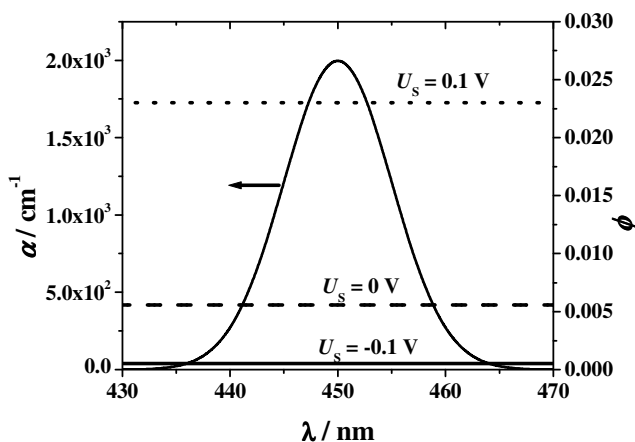


Figure 5.39 Theoretical dependencies of the quantum yield ϕ of a surface photochemical reaction involving electrons on the absorption coefficient at different surface potentials U_s (case of weak light absorption) within a hypothetical single absorption band. Reprinted with permission from Emeline *et al.*, 2003. Copyright (2003) American Chemical Society.

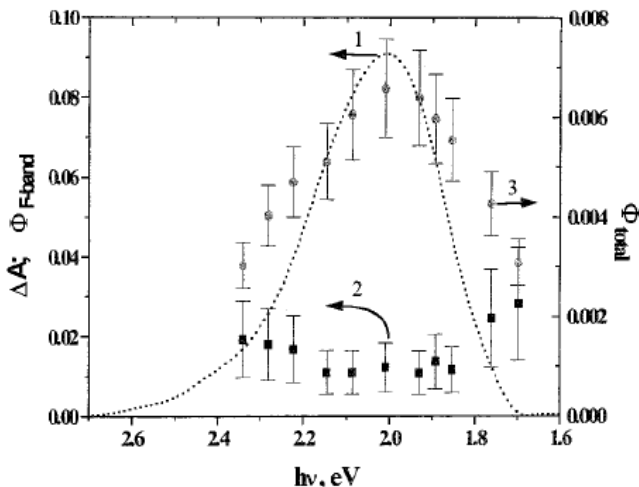


Figure 5.40 Graphic displaying the experimental absorption band of *F* colour centres in powdered KBr (curve 1) along with the experimental quantum yields at various energies for the photostimulated adsorption of O_2 (curve 2), and the total quantum yield for events occurring on photoexcitation within this *F* band (curve 3). Reprinted in part with permission from Emeline *et al.* (2000a). Copyright (2000) American Chemical Society.

The case of KBr is rather unusual in that a single absorption band of the defects existing in this solid can be selected. Typically, however, there are different types of defects in solids with overlapping absorption bands, in which case calculations of an average quantum yield ϕ_{av} necessitates using eq. 5.134.

$$\phi_{av} = \frac{R}{A\rho} = \frac{\sum_i A_i \phi_i}{\sum_i A_i} \quad (5.134)$$

where ϕ_i is a spectrally independent quantum yield corresponding to the single absorption band of a given type of defect, and A_i is the fraction of light absorbed by this type of defect.

Figure 5.41 illustrates a hypothetical single absorption band (spectrum 1) that might be composed of the overlap of two single absorption bands (curves 2 and 3) together with the calculated spectral variation of the quantum yield within the absorption band. This yields a step-like spectral dependence of the quantum yield (curve 4) (Emeline *et al.*, 1999a). An example of experimental results that follow these expectations is the case of photoinduced colour centres in ZrO_2 (curve 2; Fig. 5.42), in which the absorption bands of *F* and *F*⁺ colour centres overlap (Emeline

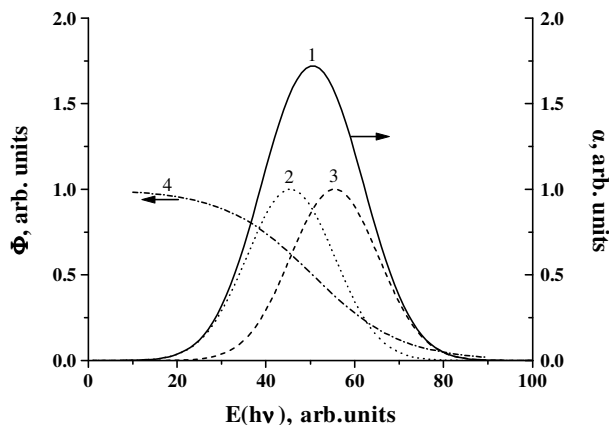


Figure 5.41 Plots showing a hypothetical single absorption band (curve 1) consisting of two overlapping bands (curves 2 and 3); curve 4 represents calculated quantum yields. Reprinted with permission from Emeline *et al.* (1999a). Copyright (1999) American Chemical Society.

et al., 2000a). The experimental quantum yields (curve 1, Fig. 5.42) are those obtained for the photostimulated adsorption of molecular oxygen on photocoloured ZrO_2 , which once again are for the case of weak light absorption. One of the bands in Fig. 5.41 (e.g. curve 3) could in principle be spectrally inactive, which according to eq. 5.134 can also result in a spectral variation of ϕ . In such a case, the corresponding $\phi_i = 0$. For example, in the photostimulated adsorption of O_2 on KBr during photoexcitation in the *F* band, the spectral dependence of ϕ transforms to a band-like dependence if the background of the inactive light absorption is taken into account (Emeline *et al.*, 1999a). Thus, in the case of weak light absorption the quantum yield is spectrally invariant within the single absorption band, and can be spectrally dependent in the case of more complex light absorption.

Figures 5.42 and 5.43 give two more examples that demonstrate, respectively, the band-like and step-like dependencies of the quantum yields for the photostimulated adsorption of oxygen, hydrogen and methane on dispersed MgO and ZrO_2 solids. The case of *strong light absorption* usually corresponds experimentally to the fundamental absorption of light by the solid photocatalyst. Accordingly we have analysed the spectral variations of the quantum yields for the case of *intrinsic* fundamental absorption, and in particular at the fundamental absorption edge of the solids.

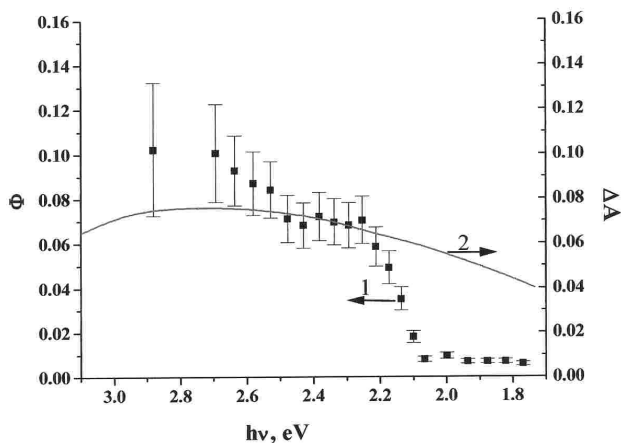


Figure 5.42 Absorption spectrum of overlapping absorptions of F and F^+ colour centres in powdered ZrO_2 (curve 2), and quantum yields of photostimulated adsorption of molecular oxygen on photoexcitation of ZrO_2 in these bands. Reprinted with permission from Emeline *et al.* (2000a). Copyright (2000) American Chemical Society.

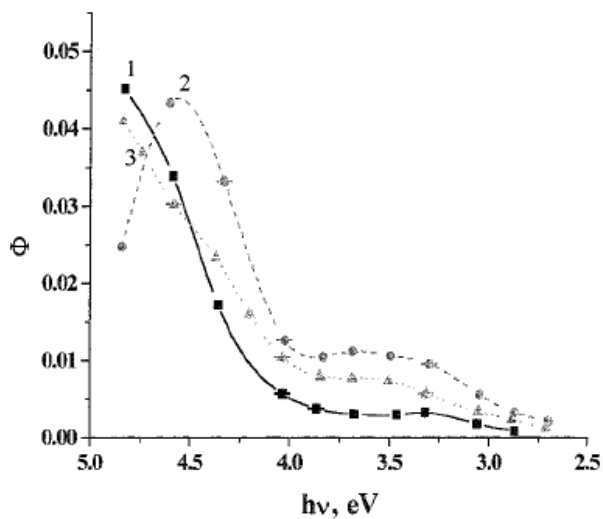


Figure 5.43 Experimental spectral dependencies of quantum yields ϕ of photoadsorption of (1) oxygen; (2) hydrogen; (3) methane on powdered ZrO_2 . Reprinted with permission from Emeline *et al.* (2000a). Copyright (2000) American Chemical Society.

Figure 5.44 displays a typical *intrinsic* absorption by a solid and the theoretical spectral dependencies of the quantum yields as a function of absorption coefficients and surface potentials (Emeline *et al.*, 2003). In essence, the theoretical quantum yields follow the step-like behaviour of the fundamental absorption, differing from each other by the value and direction of the electric field $\mathcal{E}(x)$ in the space-charge region near the surface, as reflected by the surface potential U_s .

The experimental manifestations of the spectral variations in Fig. 5.44 are illustrated in Fig. 5.45 for the photostimulated adsorption of molecular oxygen on reduced and oxidised surfaces of solid ZrO_2 . Reduction or oxidation of the surface evidently changes the surface defectiveness, and in some cases even the surface structure. The latter also affects the surface potentials and probably also the direction of the subsurface electric field.

The difference between the two curves for the quantum yields is noteworthy and corresponds, at least qualitatively, to the calculated dependences. The correspondence between the experimental and theoretical spectral dependencies seen in Figs. 5.43 and 5.44 is rather infrequent, occurring only in some very simple cases.

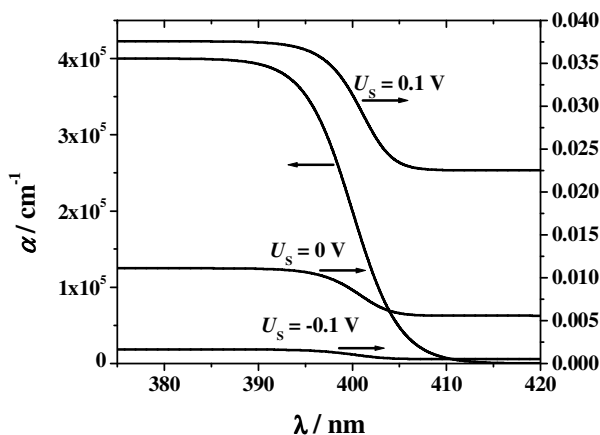


Figure 5.44 Theoretical spectral dependencies of quantum yields ϕ at the edge of the fundamental absorption for different values of the surface potential U_s ; the typical intrinsic absorption spectrum is also illustrated. Reprinted with permission from Emeline *et al.* (2003). Copyright (2003) American Chemical Society.

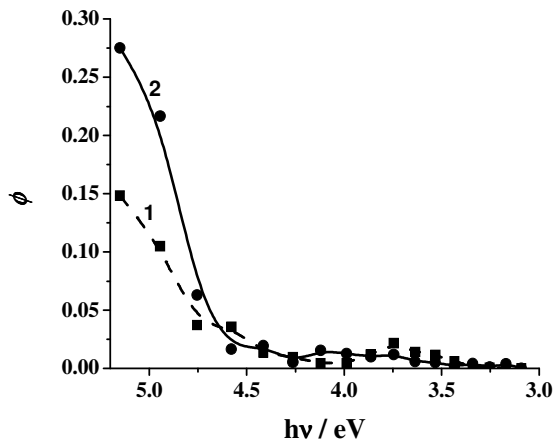


Figure 5.45 Experimental spectral dependencies of quantum yields ϕ of the photostimulated adsorption of oxygen on (1) oxidised and (2) reduced surfaces of ZrO_2 .

For more complex processes, the simple models exemplified in Fig. 5.29 and Fig. 5.36 may not explain the experimental spectral variations of quantum yields. Examples of such complex spectral dependencies are illustrated by the results shown in Fig. 5.34 for the photocatalysed degradations of phenol and 4-chlorophenol in aqueous TiO_2 dispersions (Degussa P-25), and in Fig. 5.46 for the spectral dependencies of the quantum yields of photostimulated absorptions of O_2 and H_2 on the surface of the same batch of TiO_2 . The spectral range of measurements corresponds to the spectral range of the fundamental absorption of titania. Of relevance to the earlier discussion, the maxima in the spectral dependencies of quantum yields in the latter two figures correlate exactly with the energies of indirect and direct band-to-band electronic transitions in TiO_2 (anatase form) (Emeline *et al.* 2000c) and for hydrogen adsorption to the indirect transition in the rutile TiO_2 form (Fig. 5.46, curve 2; Emeline *et al.*, 2002a). Accordingly, carriers generated from these transitions must possess different migration parameters. This contradicts the commonly accepted notion of rapid thermalisation of hot charge carriers and points to the likelihood that hot carriers photogenerated in nanoparticles can also participate in surface chemical reactions before they lose their excess energies.

In summary, it is important to recognise the role of the absorption coefficient α and the electric field $\mathcal{E}(x)$ in the subsurface space-charge region on the activity of the photocatalysts. The latter is closely connected to the surface potential, and thus to the surface structure and defectiveness, and the complexity of the surface of real particles.

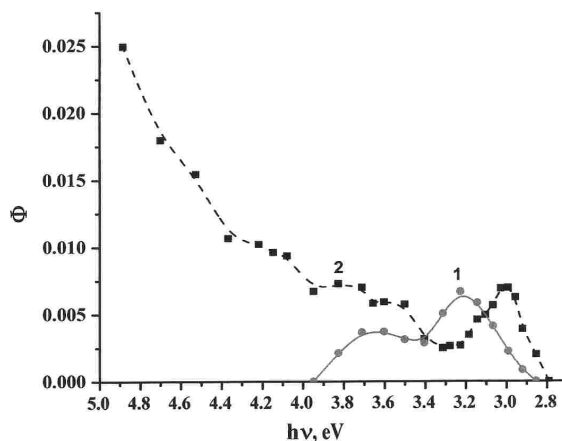


Figure 5.46 Experimental spectral dependencies of the quantum yields ϕ of photostimulated adsorption of (1) oxygen and (2) hydrogen on the surface of Degussa P25 TiO₂. Reprinted with permission from Emeline *et al.* (2002a). Copyright (2002) Elsevier Science S.A.

5.5.3 Selectivity of photocatalysts

The selectivity of a photocatalyst describes its ability to turn the reaction pathway toward certain reaction products. It can be defined as the ratio between the number of molecules of reaction products formed during the reaction and the number of reagent molecules that have been involved in the reaction. However, since the reaction rates of the degradation of the reacting substrate(s) and the formation of products can vary during the time course of the reaction, it is wise to use the ratio between the rate of formation of the i^{th} product, dN_i/dt , and the rate of the degradation (disappearance) of the reagent(s), dN_r/dt , within a given time period. Clearly, the ratio of the rates is equivalent to the ratio between the quantum yields of product formation ϕ_i and reagent degradation ϕ_r (eq. 5.135).

$$S_i = \frac{\frac{dN_i}{dt}}{\frac{dN_r}{dt}} = \frac{\phi_i}{\phi_r} \quad (5.135)$$

Another consequence of the solution to the continuity eq. 5.124 is the potential to analyse the factors that lead to the spectral selectivity of photocatalysts (Emeline *et*

al., 1999a). In particular, the ability of photocatalysts to promote either reductive or oxidative surface reactions depends on the ratio between the surface concentrations of electrons and holes (or their trapped equivalents). To the extent that surface concentrations of both types of carriers are spectrally dependent (Emeline *et al.*, 1999a), their ratio is also spectrally dependent. This can lead to spectral variation in photocatalyst selectivity. Thus far, such spectral variations of the selectivity have been observed experimentally only for a few heterogeneous systems. For example, spectral selectivity of TiO₂ was detected for the surface reaction involving (i) methane for which under *weak light absorption* TiO₂ promotes formation of complex hydrocarbons, whereas under *strong light absorption* the major pathway appears to be oxidation to CO₂ and water (Kuzmin *et al.*, 1983); (ii) 4-chlorophenol, for which at certain wavelengths the kinetics of formation and decay of the major intermediate, benzoquinone, differ significantly and were attributed to two different pathways involving electrons and holes (Emeline *et al.*, 2000c); and (iii) the reactivity of surface oxygen species adsorbed on KBr particles, which depends on whether excitation of the solid occurs in the *extrinsic* absorption region or in the excitonic absorption band (Ryabchuk *et al.*, 1989). Thus it is relevant to examine the spectral selectivity of photocatalysts more closely.

According to the simple model of surface photochemical reactions illustrated earlier (eqs. 5.114–5.117), if reductive and oxidative processes, *i.e.* interaction of reagent molecules with electrons and holes, respectively, take place only on the photocatalyst surface then the selectivity toward product formation by the reductive pathway can be expressed by eq. 5.136, and for product formation through the oxidative pathway by expression 5.137 (Emeline *et al.*, 2003).

$$S_{\text{red}} = \frac{k_{\text{red}}[e^-][M]}{(k_{\text{red}}[e^-] + k_{\text{ox}}[h^+])[M]} = \frac{\gamma}{\gamma + \frac{k_{\text{ox}}}{k_{\text{red}}}} \quad (5.136)$$

$$S_{\text{ox}} = \frac{k_{\text{ox}}[h^+][M]}{(k_{\text{red}}[e^-] + k_{\text{ox}}[h^+])[M]} = \frac{\frac{k_{\text{ox}}}{k_{\text{red}}}}{\gamma + \frac{k_{\text{ox}}}{k_{\text{red}}}} \quad (5.137)$$

Two parameters that affect the selectivity S_i stand out: (1) the ratio $k_{\text{ox}}/k_{\text{red}}$ of the rate constants for oxidation and reduction, and (2) the parameter $\gamma = [e_s^-]/[h_s^+]$ which expresses the ratio between the surface concentrations of electrons and holes.

Analysis of eqs. 5.136 and 5.137 leads to some important conclusions:

- The selectivity for reduction S_{red} increases with an increase in γ (increase in the number of surface electrons). The selectivity for oxidation S_{ox} scales with $1/\gamma$.
- The degree of variation in selectivities depends on the ratio $k_{\text{ox}}/k_{\text{red}}$.
- When $\gamma \ll k_{\text{ox}}/k_{\text{red}}$ the oxidative pathway is the favoured path.
- When $\gamma \gg k_{\text{ox}}/k_{\text{red}}$ the reductive pathway is the favoured path.

Clearly, the ratio $\gamma = [e_s^-]/[h_s^+]$ of the surface concentrations of electrons and holes is the important factor that determines the selectivity of photocatalysts.

Applying the solid plate models (Figs. 5.29 and 5.36) and the results obtained for the surface concentration of charge carriers, the behaviour of photocatalysts during photochemical reactions can be analysed. The model(s) indicates that the ratio γ is governed by various factors:

- The mobilities of the charge carriers (u),
- The lifetimes of the charge carriers (τ),
- The rates of surface recombination of the charge carriers (s), and
- The electric field $\mathcal{E}(x)$, which is perhaps the most influential factor.

The magnitude and direction of $\mathcal{E}(x)$ in the space-charge region determines the drift of the carriers of a given charge toward (or *away from*) the surface, thereby increasing (or *decreasing*) the ratio γ . The above manifestations of the selectivities S_{red} and S_{ox} are graphically illustrated in Fig. 5.47, which shows how γ and the selectivities S_i toward oxidative and reductive reaction products vary with changes in surface potentials, which in our model determine the value and the direction of $\mathcal{E}(x)$ at given constant absorption coefficients and appropriate ratios of the rate constants for

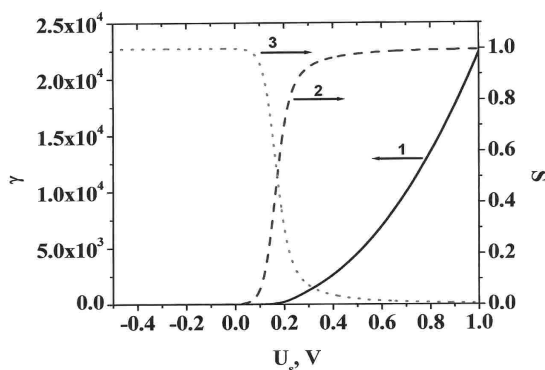


Figure 5.47 Dependencies of (1) the ratio γ between the surface concentrations of electron and holes and selectivities toward (2) reductive and (3) oxidative reaction pathways as a function of the surface potential U_s . Reprinted with permission from Emeline *et al.* (2003). Copyright (2003) American Chemical Society.

oxidation and reduction (Emeline *et al.*, 2003). Clearly, at positive surface potentials, the reaction pathway is strongly shifted toward reduction products because the electric field favours the drift of electrons toward the surface, whereas at negative surface potentials the electric field suppresses and/or prevents migration of electrons to the surface, thereby favouring the drift of holes. Although predicted by the model(s), this sort of dependence may be difficult to verify experimentally. However, other parameters that also affect the selectivity of photocatalysts can be manipulated experimentally to assess their influence on the selectivity. If experimental variations analogous to those predicted in Fig. 5.47 are observed they may be the result of surface reconstruction of the particle that can occur during heat treatment or under some other physical treatment, such as specific adsorption of ions on the surface (or in the bulk), and variation of pH of the aqueous photocatalyst dispersion. It should be noted that the surface charge is also dictated by variations of the surface structure resulting from different methods of synthesis of the photocatalytic material.

One parameter that can be manipulated experimentally is the absorption coefficient at various wavelengths for a given photocatalyst. As noted earlier in the discussion on the spectral variation of quantum yields, changes in absorption coefficient yield different surface concentrations of carriers. Accordingly, the spectral changes of the absorption coefficients with wavelength should also affect the ratio between the surface concentration of electrons and holes, which leads to the spectral variations of γ and thus the selectivity of the photocatalysts, provided that factors that govern migration of carriers are different for electrons and holes.

Figure 5.48 illustrates the theoretical spectral dependencies of the selectivity of photocatalysts for the reduction pathway on the absorption coefficient α at different surface potentials for a step-like absorption band. Dramatic variations in the selectivity of photocatalysts are expected, particularly at the fundamental absorption edge. It is relevant to ask whether there is any experimental evidence for this spectral selectivity. To investigate this, Emeline and Serpone (2002) examined the initial selectivity of Degussa P-25 TiO_2 as the photocatalyst for the formation of primary reaction intermediates in the photodegradation of phenol and 4-chlorophenol. Figure 5.49 shows our experimental findings on the initial selectivity for formation of hydroquinone, benzoquinone and catechol from the photodegradation of phenol in UV-irradiated TiO_2 dispersions measured at different wavelengths. Clearly, no selectivity was found and none was expected since phenol can only be photodegraded oxidatively by $\cdot\text{OH}$ radicals (or equivalent reactive oxygen species; under the conditions used the electrons had no effect on phenol). By contrast, the 4-chlorophenol substrate can be photodegraded oxidatively by $\cdot\text{OH}$ radicals and reductively by electrons, thereby providing possible verification of expectations.

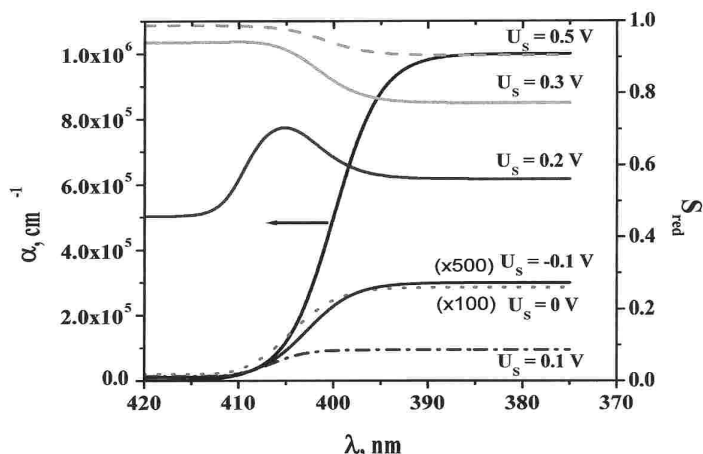


Figure 5.48 Theoretical spectral dependencies of the selectivity of photocatalysts toward a reductive pathway within a step-like absorption band at different surface potentials U_s . Note the reversal in the behaviour of S_{red} at $U_s = 0.3$ V and 0.5 V; and the band-like behaviour when $U_s = 0.2$ V due to competition between diffusion and drift of charge carriers. Reprinted with permission from Emeline *et al.* (2003). Copyright (2003) American Chemical Society.

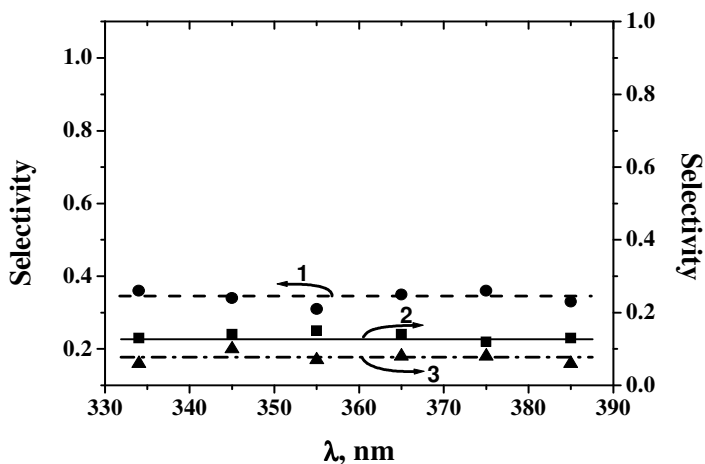


Figure 5.49 Spectral dependencies of the initial selectivity toward formation of (1) hydroquinone, (2) catechol, and (3) benzoquinone during the photocatalytic degradation of phenol over TiO_2 (Degussa P25). Reprinted with permission from Emeline and Serpone (2002). Copyright (2002) American Chemical Society.

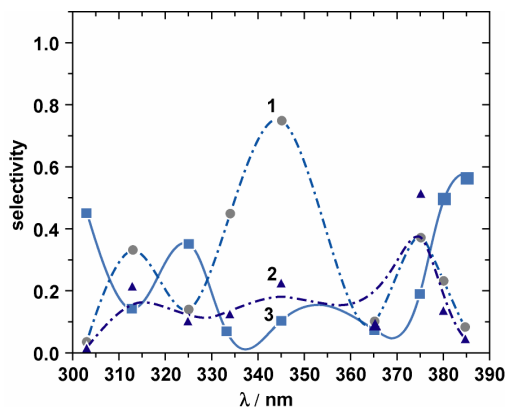


Figure 5.50 Spectral dependencies of the initial selectivity toward formation of (1) hydroquinone, (2) benzoquinone, and (3) chlorocatechol during 4-chlorophenol photocatalytic degradation over TiO_2 (Degussa P25). Reprinted with permission from Emeline and Serpone (2002). Copyright (2002) American Chemical Society.

This is demonstrated in Fig. 5.50. The scheme depicted in Fig. 5.51 (Emeline and Serpone, 2002c) illustrates the possible steps during the photodegradation of 4-chlorophenol (4-ClPhOH). Benzoquinone (BQ) is formed from interaction of 4-chlorophenol with electrons localised on the surface, whereas ClCat (chlorocatechol) is formed by interaction of the initial substrate 4-ClPhOH with the $\cdot\text{OH}$ radicals formed by hole trapping by surface OH^- groups; hydroquinone (HQ) is formed both

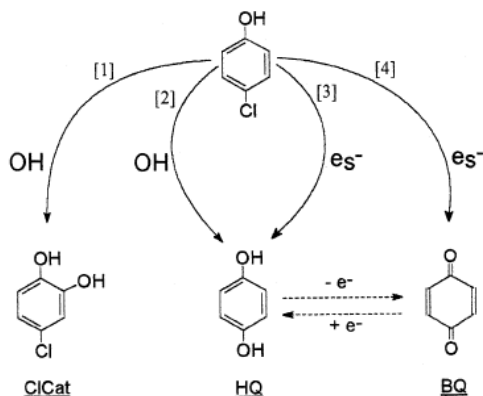


Figure 5.51 Scheme showing the proposed oxidative and reductive routes in the photodegradation of 4-chlorophenol to yield ClCat, HQ and BQ intermediates (see text). Reprinted with permission from Emeline and Serpone (2002). Copyright (2002) American Chemical Society.

reductively and oxidatively. Accordingly, the selectivity of the photocatalyst can be expressed by eq. 5.138 for ClCat and by eq. 5.139 for BQ. Clearly, both selectivities depend on the ratio γ and thus on the spectral variation of γ which causes the spectral variation of the selectivity.

$$S_{(\text{ClCat})} = \frac{k_1[\bullet\text{OH}]}{k'[\bullet\text{OH}] + k''[\text{e}^-_s]} = \frac{k_1}{k' + k''\gamma} \quad (5.138)$$

$$S_{(\text{BQ})} = \frac{k_4[\text{e}^-_s]}{k'[\bullet\text{OH}] + k''[\text{e}^-_s]} = \frac{k_4\gamma}{k' + k''\gamma} \quad (5.139)$$

By contrast, in the case of the degradation of phenol, all reaction intermediates are formed through the oxidative pathway only by reaction of phenol with the $\bullet\text{OH}$ radicals generated on the surface of the photocatalyst by hole trapping. Therefore the selectivity is spectrally invariant (eq. 5.140 and Fig. 5.49). Also noteworthy is the ratio of the two selectivities for the formation of BQ and ClCat, $S_{\text{BQ}}/S_{\text{ClCat}}$, which scales with γ (eq. 5.141). This means that the spectral variation of this ratio reflects the spectral variation of the ratio between the electron and hole concentrations on the photocatalyst surface. The ratio γ is given by eq. 5.142, where β is the ratio L_e/L_h of the diffusion lengths of electrons and holes, and B is a constant.

$$S_{(\text{PhOH})} = \frac{k_1[\bullet\text{OH}]}{k'[\bullet\text{OH}]} = \text{const} \quad (5.140)$$

$$\frac{S_{(\text{BQ})}}{S_{(\text{ClCat})}} = \frac{k_4[\text{e}^-_s]}{k_1[\bullet\text{OH}]} = (\text{const})\gamma \quad (5.141)$$

$$\gamma = \frac{[\text{e}^-_s]}{[\bullet\text{OH}]} = B \left(\frac{\alpha L_e + \beta}{\alpha L_h + 1} \right) \quad (5.142)$$

The relative photonic efficiency, ξ_{rel} , for the degradation of 4-chlorophenol over titania with respect to the degradation of phenol also scales with γ (Emeline and Serpone, 2002c). The spectral dependencies of ξ_{rel} and of the ratio $S_{\text{BQ}}/S_{\text{ClCat}}$ are illustrated in Fig. 5.52, which shows that the two dependencies correlate with each other, as expected theoretically. Again, there exists a spectral variation of γ which is reflected in the spectral variation of the selectivity of the photocatalyst.

Earlier we noted the significant spectral variation of γ and thus of the selectivity, observed at the fundamental absorption edge of the photocatalyst. Figure 5.53 shows the theoretical/simulated spectral variations of the selectivity at the fundamental absorption edge at different values of the surface potential E_s (Emeline *et al.*, 2003).

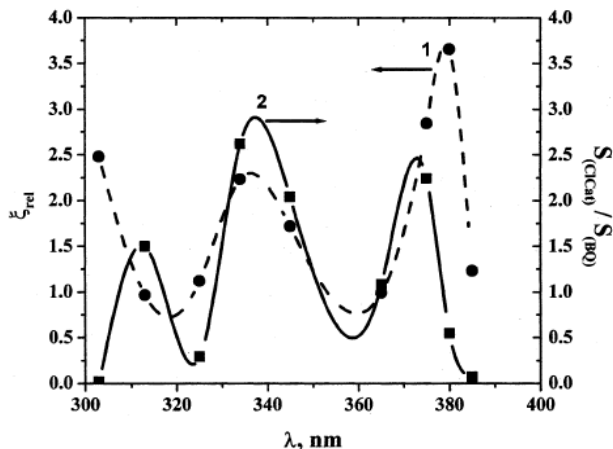


Figure 5.52 Experimental spectral dependencies of the relative photonic efficiency of the photo-degradation of (1) 4-chlorophenol and (2) S(BQ)/S(ClCat) of the ratio between the initial selectivity of the formation of benzoquinone and chlorocatechol, which scales with γ . Reprinted with permission from Emeline and Serpone (2002). Copyright (2002) American Chemical Society.

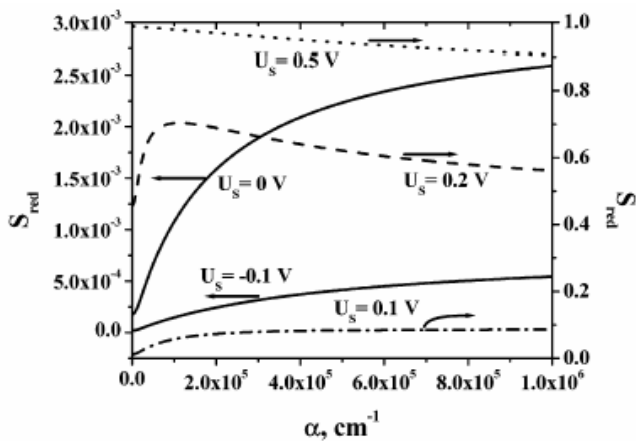


Figure 5.53 Theoretical dependencies of the selectivity of the photocatalyst toward the reduction pathway on the absorption coefficient at different surface potentials E_s . Reprinted with permission from Emeline *et al.* (2003). Copyright (2003) American Chemical Society.

Noteworthy is the increase in selectivity S_{red} with increase in the absorption coefficient α to large values. However, the more interesting feature is that for very large surface potentials, S_{red} decreases with increase in α . At $E_S = 0.2$ V, the spectral dependence of the selectivity takes on a band-like shape. This reflects the competition between diffusion and drift for transport of charge carriers to the surface. Such band-like behaviour of the selectivity finds experimental verification in the spectral dependence of selectivity at the fundamental absorption edge in the formation of benzoquinone during the photodegradation of 4-chlorophenol (see curve 2, Fig. 5.50).

Spectral variations of the ratio $\phi_{\text{O}_2}/\phi_{\text{H}_2}$ between the quantum yields for the photo-stimulated adsorption of oxygen and hydrogen, which also scales with γ , was obtained for the reduced and oxidised surfaces of ZrO_2 (eq. 5.143 and Fig. 5.54). Reduction or oxidation of the ZrO_2 surface leads to changes in the surface potentials of this metal oxide, and thus to changes in the subsurface electric field.

$$\frac{\phi_{\text{O}_2}}{\phi_{\text{H}_2}} = \frac{k_{\text{O}_2} S_{\text{O}_2} [\text{e}^-_{\text{s}}]}{k_{\text{H}_2} S_{\text{H}_2} [\text{h}^+_{\text{s}}]} = (\text{const}) \frac{[\text{e}^-_{\text{s}}]}{[\text{h}^+_{\text{s}}]} = (\text{const}) \gamma \quad (5.143)$$

Such changes are the major cause of the spectral variation behaviour as predicted by the model when ZrO_2 is photoexcited at the fundamental absorption edge. In one case, the behaviour tends to be band-like, whereas in other cases the spectral variation follows the absorption curve at the fundamental absorption edge of zirconia.

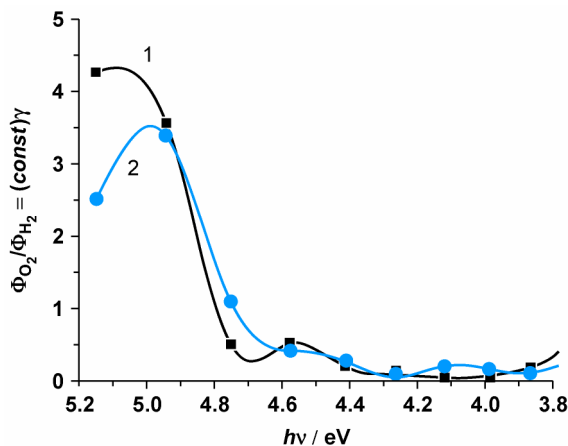


Figure 5.54 Experimental spectral dependencies of the ratio of the quantum yields of oxygen and hydrogen photo-stimulated adsorption on (1) oxidised and (2) reduced surfaces of ZrO_2 that scale with $\gamma = [\text{e}^-_{\text{s}}]/[\text{h}^+_{\text{s}}]$.

To summarise, we have described relative photonic efficiencies and quantum yields that reflect the efficiency of photons absorbed by metal-oxide particles in general, and titania in particular. On the basis of a simple one-dimensional model and predictions from the solution to the continuity equation, it was possible to examine factors that govern the spectral dependence of quantum yields. Experimental evidence has shown that surface reactions taking place on TiO_2 and on a variety of other metal-oxide systems showed spectral variations, something that was totally unexpected from the conventional band model of semiconductors. Clearly, the conventional band model of semiconductors must be viewed *cum grano salis* in light of work in the past decade by us and others. It should also be emphasised that it is not simply the spectral variation of the absorption coefficient or the magnitude of the surface potentials that affect the activity and selectivity of the photocatalysts. Rather, it is the interplay between these two. Moreover, such factors as the surface potential or subsurface electric field have too general a physical meaning as they are determined by the surface structure, surface defectiveness, surface disorder, adsorption of impurities on the surface, H^+/OH^- exchange with the surrounding aqueous phase, among other factors. Consequently, further investigations are needed to fully comprehend the factors that influence the activity and selectivity of photocatalysts.

5.6 Evidence for a gas/solid surface reaction being photocatalytic

In the last three decades or so, all studies involving heterogeneous photochemistry/photocatalysis (ours included) have always maintained that the reactions occurring on the surface of an irradiated metal-oxide specimen that acted as the light harvester and as the photocatalyst were catalytic. However, no firm experimental evidence has ever been reported to prove such an assertion. In two recent studies, Emeline *et al.* (2005a, 2005b) have provided this heretofore elusive evidence for the photoprocesses that occur in gas/solid heterogeneous systems, which involve mostly the dielectric metal-oxide ZrO_2 (zirconia), a wide bandgap material with a bandgap of $\sim 5.0\text{--}5.2$ eV.

Zirconia demonstrates significant activity in heterogeneous photochemical processes such as the photostimulated adsorption of oxygen, hydrogen and methane (Emeline *et al.*, 1998a, 1998b, 2000a), with quantum yields of 0.04–0.05, and in the photoisomerisation of 2-butene (Moon *et al.*, 1995, 1997). Photostimulated adsorption of H_2 and CH_4 occurs dissociatively, yielding $\text{H}^\bullet$ and $^\bullet\text{CH}_3$. The ultimate result of the dissociative adsorption of CH_4 is the formation of the higher hydrocarbons ethane, ethene and propane and oxidation products. EPR studies by Burukina (1990) showed that the photostimulated adsorption of O_2 yields two different forms of oxygen on the

surface of ZrO_2 particles, namely, $\text{O}^\bullet$ and $\text{O}_2^{\bullet-}$ species. The slight difference in the anisotropy of the g -factor of the EPR signal of the $\text{O}_2^{\bullet-}$ species recorded for the forms that desorbed below 370 C ($g_1 = 2.0312$) and between 370 C and 470 C ($g_1 = 2.0325$) suggested that there exist at least two different $\text{O}_2^{\bullet-}$ surface-adsorbed species on zirconia. The EPR signal of the $\text{O}^\bullet$ species was also observed after irradiation of ZrO_2 *in vacuo*, which implied that this signal was connected with hole traps on the surface and in the bulk, and was not related to any adsorbed oxygen forms. The $\text{O}^\bullet$ signal did not appear during irradiation in the presence of oxygen at liquid nitrogen temperatures. Rather the $\text{O}_3^{\bullet-}$ adsorption complex, a species that is unstable at higher temperatures, was detected. This adsorption complex is evidently implicated in oxygen isotopic exchange processes (Burukina, 1990). The surface-adsorbed superoxide anion radical $\text{O}_2^{2-\bullet}$ also formed at the thermally activated surface as a result of oxygen adsorption on Zr^{3+} and F^+ -type surface centres, produced from the thermal reduction of the zirconia surface (Zhao *et al.*, 2004).

Zirconia also displays high activity in more complex surface photochemical reactions, for instance in the photolysis of water (Sayama and Arakawa, 1996) and the photoreaction between CO_2 and H_2 (Kohno *et al.*, 2000). Although these and several other surface reactions on metal oxides (and metal halides) in heterogeneous photocatalysis have been claimed to be photocatalytic, no experimental evidence in support of their photocatalytic nature has ever been demonstrated.

As we noted earlier in this chapter, the term *heterogeneous photocatalysis* has been widely used to describe photochemical events in gas/solid and liquid/solid heterogeneous systems involving, in most cases, metal oxides as the photocatalysts (Serpone and Pelizzetti, 1989; Zamaraev and Parmon, 1991; Fox and Dulay, 1993; Hoffmann *et al.*, 1995; Linsebigler *et al.*, 1995; Fujishima *et al.*, 2000; Matsuoka and Anpo, 2003; and references therein). In many studies, however, the nature of processes as being photocatalytic has been inferred and was not based on firm experimental evidence. The problem originates, at least in part, because no official description of heterogeneous photocatalysis and its characteristics has yet been formulated despite attempts to provide a basis for discussion (Parmon, 1997; Serpone and Emeline, 2002). In these earlier studies (see also Serpone *et al.*, 2000), attention was focused on describing heterogeneous photocatalysis and photocatalysts so as to establish experimental procedures/protocols to help clarify the catalytic nature of a given photochemical process in heterogeneous systems.

As we described in Section 5.2.5, considering photocatalysis as a branch of catalysis allows an expansion of the rules that normally apply in general catalysis to photocatalysis. In particular, the photocatalyst must be restored to its original chemical and thermodynamic state at the end of the photoreaction. Moreover, the

photocatalyst must alter the reaction pathway so as to reduce the activation energy of the photoreaction. For example, the photocatalyst typically sensitises the photochemical reaction to photons of lower energy than are needed by the corresponding homogeneous photochemistry. Consequently, to characterise photochemical events in heterogeneous systems, parameters from both photochemistry and catalysis must be invoked. Quantum yield and photonic efficiency are two such terms borrowed from photochemistry, both being used to estimate the relative activity of photocatalysts; *i.e.* the ability of a photosystem to transform photon energy into one or more chemical sequences. However, we need to recognise that both photochemical parameters are silent as to whether or not a photoprocess in a heterogeneous system is actually photocatalytic. Only for an ideal stationary photocatalytic process does the quantum yield (and thus photonic efficiency) remain constant in time. In practice, however, any chemical or physical secondary process can alter the value of ϕ , thus making it kinetically variable. Accordingly, only parameters borrowed from the field of catalysis can answer the question as to whether or not a given photon-induced process is photocatalytic. One such parameter is the turnover number (Serpone *et al.*, 2000) which, as we noted earlier, poses no difficulty in homogeneous photocatalysis. When this parameter exceeds unity, the photoreaction is said to be photocatalytic, regardless of secondary events/reactions that may accompany the process. Otherwise, the photoprocess represents simply a stoichiometric heterogeneous photoreaction.

In the first recent study, Emeline *et al.* (2005a) studied the photooxidation of hydrogen in the presence of molecular oxygen over irradiated powdered ZrO_2 , presenting experimental evidence that this photooxidation reaction and the concomitant photoadsorption (*i.e.* photoreduction) of oxygen when both gases are present in the heterogeneous system are truly photocatalytic. To demonstrate this it was imperative that the turnover numbers (TON)⁶ of the photoprocesses be ascertained. However, if surface-active centres are blocked by reaction intermediates or products, or if the photostimulated adsorption of gases is the only photoprocess that takes place, then TON will probably not exceed unity. It is well known in the field of catalysis that a reaction is catalytic if it can be shown that the turnover number is greater than unity. Hence, for a reaction to be described as photocatalytic in photocatalysis, the TON for the surface reaction occurring on a photocatalyst must also be greater than unity (Serpone *et al.*, 2000; Serpone and Emeline, 2002).

⁶ Turnover number (TON) refers to the ratio of the number of photoinduced transformations for a given period of time to the number of photocatalytic sites (or centres) in heterogeneous photocatalysis, or to the number of photocatalyst molecules in homogeneous photocatalysis. TON is a dimensionless quantity (see Section 5.2.6 and also Serpone and Emeline, 2002).

Determination of TON requires an estimate of the number of surface-active centres that participate in the reaction on the metal-oxide surface. This has represented a most challenging problem in heterogeneous photocatalysis because heretofore there has been no description of the nature, nor a quantitative determination of the number, of active centres in heterogeneous photocatalysis, and their concentration on the surface of a metal-oxide photocatalyst remains elusive. To complicate matters further, there is also some uncertainty about how much of the surface area of the metal-oxide photocatalyst is irradiated by the incident actinic light, and can therefore be active in photocatalysis. Accordingly, even if the concentration of active centres were known, it would normally be difficult to estimate the number of those centres actually involved in the photochemical events.

To overcome some of these challenges, Emeline and co-workers (2005a) used three approaches to determine the TON of the photoreaction between hydrogen and oxygen over irradiated zirconia. The first was based on the known value of the post-irradiation adsorption coefficient (henceforth termed post-adsorption; Polikhova *et al.*, 2004) and the application of diffuse reflectance spectroscopy (DRS) to determine the number of long-lived surface-active centres for the post-adsorption of molecular oxygen. Figure 5.55 shows the difference DRS spectrum corresponding to absorption by surface centres for the post-adsorption of O₂. Using the absorption coefficient determined by Burukina and co-workers (1990a, 1990b) for ΔR at $\lambda = 650$ nm for ZrO₂, the number of colour centres was estimated to be $\sim 1 \times 10^{15}$ (eq. 5.144).

$$N = \frac{\Delta R_{650\text{nm}}}{4.7 \times 10^{-18}} = 1 \times 10^{15} \text{ centres} \quad (5.144)$$

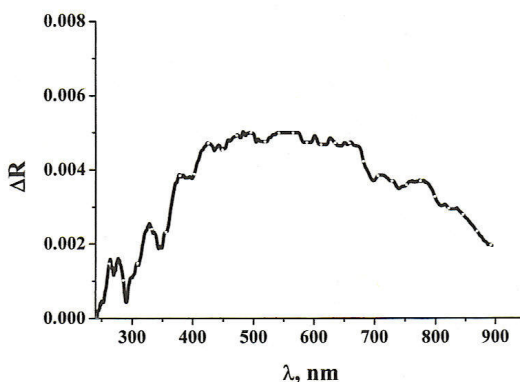


Figure 5.55 Difference DRS spectra corresponding to the absorption of long-lived active centres in the post-adsorption of oxygen. Reprinted with permission from Emeline *et al.* (2005a). Copyright (2005) American Chemical Society.

In the study by Polikhova *et al.* (2004), the coefficient of post-adsorption of oxygen η at $t \rightarrow \infty$ was 0.1 (eq. 5.145).

$$\eta = \frac{N_{\text{post-ads}}}{N_{\text{photo-ads}}} = 0.1 \quad (5.145)$$

where $N_{\text{post-ads}}$ is the number of long-lived centres for the post-adsorption of oxygen and N_{photoads} denotes the total number of surface-active electron centres (both long-lived and short-lived). Accordingly, the total number of surface-active centres⁷ is given by $1 \times 10^{15} / \eta = 1 \times 10^{16}$ (for details see Emeline *et al.*, 2005a).

The second approach was based on the determination of the number of post-adsorbed oxygen molecules from the thermoprogrammed desorption (TPD) spectrum, estimated as 9.4×10^{14} at sufficiently long irradiation times (Emeline *et al.*, 2005a). Assuming that one adsorbed molecule occupies one surface-active centre, and taking into account the coefficient of post-adsorption $\eta = 0.1$, the total number of surface-active centres was 9.4×10^{15} , in fairly good agreement with the first approach that gave 1×10^{16} such centres.

In the third approach, the total number of surface-active centres was obtained by extrapolation of the kinetic curve that represents the accumulation of photoadsorbed oxygen species obtained from the TPD spectra (see Fig. 5.56). This gave 8.8×10^{15} such centres at the limit of $t \rightarrow \infty$, corresponding to the maximal number of surface-active centres, also in fair accord with the above estimates.

The change in oxygen pressure during the photoreaction of the components in the gas mixture over zirconia corresponded to $\sim 6.2 \times 10^{16}$ oxygen molecules (M_{O_2}) that were involved in all the photoprocesses taking place at the surface of zirconia. Consequently, after 6000 s of irradiation the TON is given by

$$\text{TON} = \frac{M_{\text{O}_2}}{N} = \frac{6.2 \times 10^{16}}{9.4 \times 10^{15}} = 6.6 \quad (5.146)$$

This suggests that on average about 6.6 molecules of oxygen react with the same surface-active centre during the time course of the photoreaction. Note that the TON for the photoadsorption of oxygen is greater than unity, as required for the process to be photocatalytic.

⁷ The total number of surface colour centres of a given type, and hence surface-active centres (here of the electron type for adsorption of oxygen), is a dimensionless quantity since it also represents the product of the number of regular surface sites per cm^2 of surface multiplied by the surface area in cm^2 of the specimen (Serpone and Emeline, 2002).

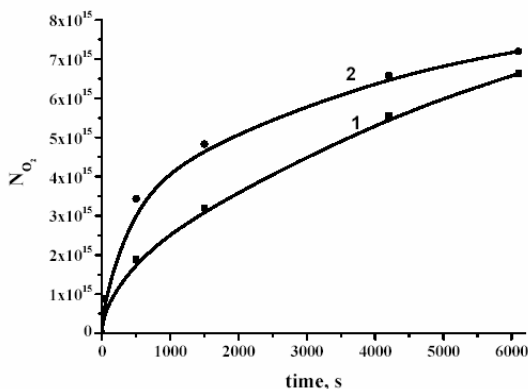


Figure 5.56 Number of molecules of oxygen accumulated at the surface of zirconia as a function of irradiation time during the (1) photoinduced adsorption (reduction) of oxygen, and (2) the photooxidation of hydrogen. Reprinted with permission from Emeline *et al.* (2005a). Copyright (2005) American Chemical Society.

Assuming that the total number of surface-active centres for hydrogen is about the same as for oxygen, and taking into consideration that 1.4×10^{17} hydrogen molecules were involved in the reaction, Emeline and co-workers (2005a) estimated TON for hydrogen to be 14.5. This means that on average about 14.5 molecules of hydrogen reacted with the same surface-active centre during the experimental time (100 min) of the photoreaction. Again the TON is greater than unity. Accordingly, the nominal photoreactions between the components of the H_2/O_2 gas mixture over powdered zirconia are truly *photocatalytic processes*.

As evidenced by the TPD data and the kinetics of oxygen accumulation on the surface, the photostimulated adsorption of oxygen was a significant secondary process and the most likely factor responsible for the rather low value of TON in the overall photooxidation of H_2 in the presence of O_2 . The same is true with respect to the photostimulated adsorption of hydrogen. Another factor that can diminish the TON value is the non-uniformity of irradiation of the zirconia specimens. In this regard, because of strong light absorption, the accumulation of oxygen on the surface may already have been saturated so that its photocatalytic reaction with hydrogen may have reached a stationary rate. By contrast, the photoreactions of the gases in the inner layers of the powdered zirconia specimen might still have been in the initial stages of accumulation. Thus, the estimates of turnover numbers reported by Emeline *et al.* (2005a) for the two photoprocesses represent lower limits, and do not correspond to actual TON values. This notwithstanding, even these lower limits confirm that the photoprocesses examined are indeed photocatalytic.

A non-photocatalytic reaction occurring on the surface of an irradiated wide bandgap metal oxide such as ZrO_2 can also affect the process of photoinduced formation of Zr^{3+} , *F*- and *V*-type colour centres. The effect of such reactions is seen as the influence of photostimulated adsorption on the photocoloration of the metal-oxide specimen. Photoadsorption of electron donor molecules leads to an increase of electron colour centres, whereas photoadsorption of electron acceptor molecules leads to an increase of hole colour centres. Monitoring the photocoloration of a metal-oxide specimen by DRS spectroscopy during surface photochemical reactions can provide a further opportunity to evaluate whether the reactions are photocatalytic.

In a subsequent study, Emeline and co-workers (2005b) examined the influence that simple photoreactions might have on the photocoloration of ZrO_2 . Such reactions include the photostimulated adsorption of molecular oxygen and the photostimulated adsorption of hydrogen (separately present in the heterogeneous system), the photooxidation of H_2 in the presence of adsorbed O_2 , the photooxidation of NH_3 and the photoconversion of CO_2 . TPD and mass spectral monitoring of the photo-reaction involving NH_3 identified hydrazine, N_2H_4 , as an intermediate species and molecular N_2 as the final product. From these results we concluded that the photo-oxidation of NH_3 and the photoinduced events involving CO_2 are *non-photocatalytic*, unlike the photooxidation of hydrogen, which is *photocatalytic* in the presence of oxygen. Carbon dioxide ($\text{CO}_2^{\bullet-}$) and carbonate ($\text{CO}_3^{\bullet-}$) radical anions formed by interaction of CO_2 with Zr^{3+} centres and surface hole states (*i.e.* $\text{O}_s^{\bullet-}$), respectively.

In summary then, the two studies of Emeline *et al.* (2005a, 2005b) have demonstrated that for a true photocatalytic process occurring on a metal-oxide photocatalyst, two conditions must be satisfied:

- The rates of consumption of charge carriers in the reduction and oxidation half-reactions must be equal to each other (note that the condition imposed by Fig. 5.11c applies to any photocatalyst);
- The photocoloration of the metal-oxide specimen must achieve the limits of accumulation of hole and electron colour centres where the number of electrons trapped by the solid's defects equals the number of trapped holes.

The latter condition corresponds to the requirement that the photocatalyst must return to its original state at the end of the reaction cycle. Any deviation from these two conditions will point to a *non-catalytic nature* of the surface photochemical process. In this regard, the effect of non-photocatalytic reactions such as the photostimulated adsorption of O_2 and the photostimulated adsorption of H_2 on the colouration of a metal-oxide specimen can be used as a benchmark to estimate the extent to which a surface photoreaction deviates from being truly photocatalytic.

5.7 Concluding remarks

In this chapter we have attempted to retrace the development of the fundamental science that underlies heterogeneous photocatalysis *in a chronological manner* as we collectively progressed, with most of it relying on metal oxides as the photocatalysts and our own work as the stage. A greater understanding of heterogeneous photocatalysis in particular, and advanced oxidation processes in general, have lagged far behind the reports of degradation of organic polluting substances (to be reported in Vol. IV of this series). These studies began in earnest in the late 1970s and early 1980s when the conversion of solar energy to chemical energy was the proverbial 'bandwagon'. These studies focussed in large part on the water-splitting reaction. Some success was achieved, but the yields of hydrogen and oxygen were disappointingly low (less than 1% to 2 % at best), even in the presence of sacrificial electron donors, usually organic substances, to tie up the valence-band holes so that the photogenerated electrons could do their work in reducing water. It was the realisation that the organic electron donors could be oxidised to carbon dioxide that led several workers to follow the environmental photochemical route to attenuate pollution in many ecosystems (air, water and soil). In the early 1990s, we recognised that we needed to understand the details of the 'photocatalytic' process from both the material side and from the events that took place at the photocatalyst surface and at the interface in gas/solid and liquid/solid heterogeneous systems. For instance, why were the efficiencies of water splitting so low? Was electron/hole recombination too fast for the necessary chemistry to compete effectively? What was the so-called valence-band hole that did most of the oxidation of the organic substrates? Did the primary reactions take place at the surface of the photocatalysts, or did the oxidising entity desorb from the surface and oxidise substrates in the solution bulk in liquid solid systems? These and other considerations formed the basis for our investigations of the details of the photocatalytic processes in heterogeneous media.

After a brief introduction, the chapter addressed the optical properties of the photocatalysts (mostly chalcogenide semiconductors), as particles of nanometre size in colloidal solution. Since the notion in the photodegradation of organic pollutants has been that the processes are photocatalytic (without much evidence to confirm this), we then discussed the nature of photocatalysis and turnover quantities, noting the uncertainties that arose because of the long-standing lack of knowledge of the nature of surface-active sites and the number of such sites on the photocatalyst. This has also been a long-standing issue in heterogeneous (thermal) catalysis. In photocatalysis, this issue is rendered even more problematic because of the action of the photons on the photocatalyst materials.

To systematise the many discrepant reports on process efficiencies and viewpoints from many laboratories, we next examined several strategies to define a parameter for process efficiencies, ending up with an experimental protocol to determine process quantum yields described with the same rigour as in photochemistry. To assess what factors govern the photocatalytic process, we described modelling of photoinduced events after our discovery of spectrally (wavelength) dependent quantum yields and the spectral selectivity of events on metal-oxide photocatalysts. Both the experimental results and the modelling have led us to question the conventional model of semi-conductors with regard to fast thermalisation of photogenerated hot charge carriers. Finally, our recent methodologies to assess the number of active sites on a photocatalyst surface and thus determine turnover numbers, together with considerations of what constitutes a return of the photoactivated photocatalyst specimen to its original ground state, have allowed us to conclude that some of the events taking place in 'heterogeneous photocatalysis' are photocatalytic and some are not. Further studies need to focus on some of the remaining issues that have been raised implicitly and explicitly throughout the chapter. Some of these will be addressed in a forthcoming review by ourselves and others (Serpone *et al.*, 2008).

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INORGANIC EXTENDED-JUNCTION DEVICES

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*One does not discover new lands without consenting
To lose sight of the shore for a very long time.*

André Gide, Les Faux-Monnayeurs, 1925.

6.1 Introduction

The development of electronic devices is heavily reliant on the preparation of materials with low defect densities. High-purity precursor materials and a variety of elaborate processes, such as gettering, annealing and surface passivation, are necessary to obtain high material quality for electronic applications. For large-area devices, this approach has a significant effect on fabrication time, energy and cost. This is particularly relevant for solar cells, whose competitiveness ultimately depends on just these factors. Materials development is therefore a particularly important part of our way towards large-scale photovoltaics. It may nonetheless be useful to explore alternative routes towards device optimisation, particularly those which appear complementary to the general materials science scheme and which more specifically address the needs and requirements of photovoltaic devices. Thus, while the optimisation of electron transport is important in most semiconductor applications and is targeted in much conventional material development work, it is an often-neglected fact that in photovoltaic applications slow transport and—under certain conditions— even short-range transport can be acceptable in solar cells. Therefore from a very general viewpoint, it would appear desirable to explore solar cell configurations and growth processes that accommodate these less stringent requirements.

Here we intend to show that this type of approach may indeed hold considerable innovation potential. This chapter focuses on the exploration of a novel type of solid-state solar cell whose main ingredient is a non-planar geometry that permits a substantial reduction of material, the implementation of inexpensive processes in fabrication and an increased tolerance of non-optimum electronic properties. The central design goal is the implementation of a short collection path length for the photogenerated carriers and a longer optical path for the incoming photons. By a short collection path we mean a short transport distance for electrons and holes from their generation site to the collecting contact layer. If the transport distance is small, then the mobility–lifetime product in the absorber can be small, or conversely, the electronic material quality may be low, and low-cost approaches in the fabrication of solar cells may become feasible. By a longer optical path we mean an enhancement of the optical path length in the cell through reflection and scattering. By this means the absorptance of the cell is increased, a smaller amount of absorber material is necessary, and, in addition, the transport distances are even further decreased. While this approach appears particularly promising for photovoltaic applications, surprisingly, it also holds interest for other electronic applications such as transistors, sensors and LEDs. At the end of this chapter we will therefore briefly mention these applications outside the photovoltaics field.

From a basic point of view, the semiconductor in the solar cell serves two functions: to absorb a large portion of the incoming sunlight in electronic excitation processes, and to effectively transfer the photogenerated excess carriers into the external circuit. These functions largely depend on the optical and electronic properties of the material, but they are also closely linked to the cell geometry, as can be illustrated in two examples: in the conventional crystalline silicon cell a simple planar geometry is used, and this leads to very stringent requirements on the carrier transport properties. Due to the low absorptivity of Si in the peak region of the solar spectrum, a cell thickness of approximately 200–300 μm is required. Collection of the photoexcited carriers involves mainly diffusive transport. Therefore material with diffusion lengths of $\sim 200\text{--}500 \mu\text{m}$ is needed to ensure loss-free carrier collection. While the challenge of transporting excited carriers over such large distances can indeed be met (see, for example, Voss *et al.*, 1998), the development of the necessary technical know-how has taken several decades. It is probably fair to say that the material development towards these impressive electronic parameters would not have been possible within the field of photovoltaics alone, but was largely driven by other electronic applications. With the accumulated knowledge in the Si field, the material is presently in a dominating position in photovoltaics. But it is thought by many experts that, despite the fortuitous development in the Si field, the conventional

silicon solar cell will be too costly in terms of energy, material and processing time to be the basis of large-scale production of energy.

The development of the dye-sensitised solar cell is indicative of a different route towards the solution of the transport problem in solar cells. The emergence of this cell type over recent decades (Gerischer *et al.*, 1968; Desivestro *et al.*, 1985; O'Regan and Grätzel, 1991) has demonstrated that materials with very poor transport properties also have a chance in photovoltaics. In fact, in this development it became clear that carrier diffusion or drift lengths as small as a few Ångströms may be sufficient when the device design is appropriately configured (Grätzel, 2000). The absorber material of the dye cells consists of large organic molecules with a strong absorption band in the visible spectral region (Nazeeruddin *et al.*, 2001; Nazeeruddin and Grätzel, 2002). Typically a 500 Å thick dye film is able to absorb 80% of visible solar light. However, the excited state of the adsorbed dye molecules is spatially localised and carrier transfer is restricted to the Ångstrom scale. Thus there is little chance to extract the photogenerated carriers out of an absorber layer, even if it is only 500 Å thick, less than one thousandth of typical Si wafer thickness. This problem was solved by O'Regan and Grätzel (1991), who used a cell geometry in which the absorber is spread across the enlarged surface area of a highly porous substrate. By this means the local absorber thickness could be decreased to a molecular monolayer, *i.e.* so much that the necessary transport distance within the absorber was reduced to what the absorber material was capable of providing: transport over a few Ångströms—essentially the extent of the molecule. Since the porous geometry of the substrate produced a folding of the molecular layer by several hundred times, the total absorbance could be made sufficiently high. With hole transport provided by a liquid electrolyte, energy conversion efficiencies of more than 11% have now been achieved; with solid electrolytes the efficiency is now about 5% (see Fig. 1.2).

The two device approaches are thus sending an interesting message. On the one hand the Si example shows that materials development can go a very long way, when it is pursued rigorously. On the other hand, the dye solar cell development shows that there are ways around the often-intimidating materials challenges: a change in the geometric design allows reduction in the necessary transport paths by as much as a factor of 10^6 .

Figure 6.1 illustrates typical absorber thicknesses in today's solar cell technology. A vast range of absorber layer thickness is covered in practical devices, with the crystalline Si cell and the dye cells at the extreme ends. Thin-film cells, among them amorphous and microcrystalline Si:H cells and the compound semiconductor cells, lie in the range between 500 nm and 5 μm . This is still two orders of magnitude above the dye layer thickness! While optical light trapping, antireflection coatings and

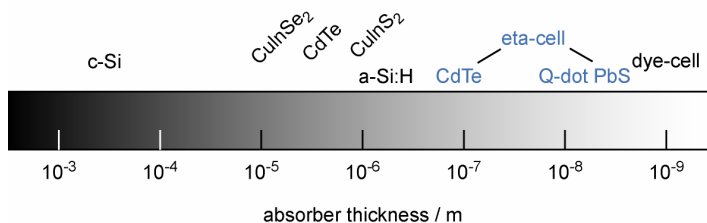


Figure 6.1 Absorber thickness in today's solar cells as compared with the thickness of extremely-thin-absorber cells (ETA cells) using CdTe or quantum dot PbS absorbers.

multijunction designs are exploited in many of today's devices and have helped to reduce the cell thickness, it appears that there is still plenty of scope for a further reduction in the absorber thickness.

This chapter discusses recent research efforts in highly non-planar design geometries in all-solid-state inorganic solar cells. The underlying goal in this work has been the reduction of the necessary transport path in those regions of the cell where the main losses occur. In many cases this is the absorber layer, where excess electrons and holes are present in close proximity and the recombination rate can be very large. In other regions of the cell, where majority-carrier transport prevails, excess carriers have a much longer lifetime and therefore larger transport distances are more easily achieved. In these regions a reduction of the transport path is not really necessary—on the contrary, in the majority-carrier regions even longer transport distances are permissible. The promise of these highly non-planar solar cells is that absorber materials with mediocre electronic properties can be used, implying that less expensive and possibly even new materials can be employed in device fabrication, or that less expensive processes can be used. The intimate relationship between thickness, transport length and absorptivity has already been noted: essentially the absorptivity sets the thickness of the solar cell, and—in a planar cell—the thickness equals the transport distance. In non-planar cells, the geometry can be looked upon as a new variable in the game. It can be used to change the required transport distances in one or more parts of the cell and thereby optimise the performance for given transport parameters. Thus, if it turns out that some inexpensive thin-film material can be prepared with diffusion lengths around 100 nm, while on the basis of its absorptivity an optical thickness of $1.5 \mu\text{m}$ is required, one would aim to explore cell geometries that reduce the absorber layer thickness locally by a factor 15 and provide an area enhancement by approximately the same factor.

The work reported in this chapter appears to indicate that these and larger values for the reduction of the absorber thickness can indeed be realised with inexpensive substrate and absorber materials. Given the early stage of this research and the as yet limited theoretical understanding of non-planar devices of this kind, the emphasis in this chapter will be on experimental results and qualitative concepts.

In the next section we will discuss the basic design rules for a non-planar, solid, inorganic solar cell with an extremely thin absorber layer. This type of cell has often been called the ETA cell (for **e**xtremely **t**hin **a**bsorber; Ernst *et al.*, 2000) or ETA cell, and we will use the latter acronym here. Materials aspects, structural, electronic and optical considerations will be introduced.

One of the basic challenges in the fabrication of highly non-planar devices lies in the preparation: only a few methods have so far been explored to produce deeply structured thin films on a flat substrate and—in a second step—to produce a continuous coverage on a deeply structured substrate. In Section 6.3, some of the possible fabrication processes will be discussed.

The focus will be on simple chemical and electrochemical preparation methods for substrate and functional layers. The experimental work indicates that highly structured morphologies can be obtained using low-cost techniques suitable for large-area coverage. Furthermore, it will be pointed out that simple chemical techniques allow a manipulation of morphologies on the sub-micron scale and a morphology transfer from one material to another. Structuring, deposition, manipulation and transfer of morphologies can be considered the basic processes in this type of device fabrication, and the demonstrated feasibility of these techniques is therefore very important.

Electronic and optical properties of structured thin films and heterojunctions are treated in Section 6.4. Since non-optimal electronic properties are to be accommodated in the new cell design, the transport properties to be discussed will naturally be those of defect-rich materials.

Experimental and theoretical performance results on prototype devices are presented in Section 6.5. So far only very few cells have been successfully fabricated. Different non-planar geometries and a variety of absorber and substrate materials will be discussed. Finally, in Section 6.6, a critical assessment of the state of the art of these new devices and an outlook on future research, including applications beyond the photovoltaic field, will be given.

6.2 Concepts for extremely thin absorber cells

6.2.1 Structure and operation

Figure 6.2a shows a schematic diagram of a non-planar solar cell with porous geometry. This cell consists of a thin intrinsic or lightly doped absorber layer embedded between two transparent transport layers, which themselves border on two planar contact layers. The transport layers serve the purpose of transferring the photogenerated carriers from the absorber layer towards the contacts and are not meant to contribute to the light absorption. Their role is mostly to accommodate the highly structured absorber and ensure carrier transfer to the contact layers under majority-carrier transport conditions. Accordingly, the transport layers must be transparent and at least slightly doped *p*- or *n*-type. The interface between the transport and contact layers is planar, and the contact layers have near-metallic

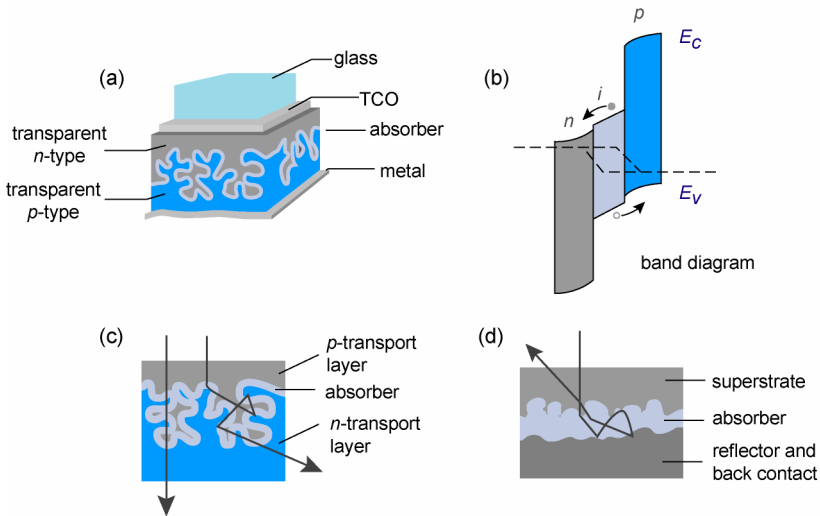


Figure 6.2 Schematic diagram of solar cells with extended junctions and an extremely thin absorber: (a) Layer structure for a superstrate *n-i-p* cell: in this configuration a highly structured *n*-layer is deposited on a transparent conductive oxide (TCO) contact layer, then a conformal absorber layer is deposited, followed by a transparent *p*-type transport layer and finally a reflective metal contact; (b) Band diagram for the *n-i-p* heterojunction. The valence-band edges (E_V) and conduction band edges (E_C) for the absorber and transport layers and the electron and hole quasi-Fermi levels are shown; (c) Illustration of reduced transport paths in the absorber layer and extended optical paths due to scattering in the heterostructure; (d) Extremely thin absorber cell with a comparably shallow structure and a metal back contact in place of a transparent transport layer.

conductivities; they have to be transparent on the light-entry side and reflective on the backside. The figure shows an example of a superstrate $n-i-p$ cell. In this arrangement the absorber is deposited on a porous n -type substrate layer that serves as an electron-transport layer. This transport layer is in turn deposited on a strongly n -doped transparent conductive oxide layer on glass. The back contact consists of a transparent p -type transport layer and a metallic, optically reflective metal film. This is, of course, only one out of several choices for the cell structure. Illumination through the substrate or the top layer are both possible, and the deposition sequence can be $n-i-p$ or $p-i-n$. However, materials aspects seem to limit these choices somewhat. Most deeply structured films have been made of n -type oxides, most prominently TiO_2 and ZnO . Since TiO_2 and ZnO can produce majority-carrier transport conditions only for electrons, and since they are also highly transparent over most of the solar spectrum, it appears advantageous to use these materials on the light-entry side. As a consequence, the superstrate $n-i-p$ structure has mostly been pursued.

The operation of the cell is illustrated in Figs. 6.2b and c: the band alignment of the transport layers with respect to the absorber and the electric field across the absorber is such that fast separation of the photogenerated carriers is supported. Electrons will be driven towards the n -type transport layer and subsequently to the n -contact, while holes can only enter the p -transport layer and then reach the p -contact. As the absorber layer is embedded between two transparent transport layers, a light ray can pass through the highly folded absorber several times. The local absorber thickness in this configuration is therefore thinner than the total optical thickness.

To a first approximation, the local thickness is inversely proportional to the surface enlargement of the substrate when the total volume of the absorber remains constant. Thus the reduced absorber thickness comes at the cost of an enlarged interface area. When strong optical and electrical losses occur at the interfaces, this trade-off may be somewhat problematic. For such conditions, the large interface area may produce strong recombination or absorption losses, and a more compact design with reduced, rather than increased, interface area would be desirable. If interface losses cannot be avoided, the ETA cell design does not make much sense. In other cases, however, particularly when bulk recombination constitutes the main loss mechanism, a reduced transport path length will be advantageous.

When the total device thickness is to remain in the micrometre regime, and a sizeable surface enlargement is to be obtained, the feature size of the substrate structure needs to be in the micrometre region or below. One is hence looking for substrate structures that provide a micro- or nano-scale pattern. For photovoltaic applications this pattern, and the necessary manufacturing processes, must be extendable over very large areas. New deposition techniques which provide

conformal and void-filling coverage need to be developed for the deposition of absorber and transport layers. If the substrate morphology is porous, as shown in the figure, the transport layers need to be transparent to avoid shadowing effects. When the structuring of the cell is not very deep, it is often possible to use a non-transparent transport layer on the rear side of the cell. In these cases the transparent transport layer can be replaced by a metallic contact, as shown in Fig. 6.2d. Experience shows that the omission of a transparent back contact strongly simplifies the fabrication of these heterojunction solar cells, and much work has therefore been geared towards these shallower structures.

6.2.2 Transport considerations

When the electric field is sufficiently strong and the transport is field-assisted, the transport path length d depends on the carrier mobility u , the recombination time τ , and the field strength $\mathcal{E}$, and is given by $d = u\tau\mathcal{E}$ (Rose, 1978). When the field is only weak and diffusion conditions govern carrier transport, the transport distance is essentially given by the diffusion length, $d = (u\tau kT/q)^{1/2}$. The mobility–lifetime product $u\tau$ is the critical material parameter in both cases. Simple considerations show that in the case of very small $u\tau$ products, diffusive transport is usually more effective. Assuming $u\tau = 10^{-10} \text{ cm}^2 \text{ V}^{-1}$, a typical low value in nanocrystalline or amorphous materials, it is seen that the diffusion length is 300 nm, while a drift length of that magnitude would require an electric field of $3 \times 10^5 \text{ V cm}^{-1}$ and a potential drop of 10 V along the transport path, which cannot be reached in a moderately doped p – n junction. Thus diffusive transport usually dominates in ETA cells.

Depending on the details of the carrier distributions and densities, majority and minority carrier parameters have different importance. Under ambipolar transport conditions, which often hold in solar cell operation, the ambipolar $u\tau$ product is the relevant transport parameter. This has a somewhat complicated dependence on the minority- and majority-carrier parameters, but in many cases it can be approximated by the minority-carrier $u\tau$ product. However, when the absorber material is not sufficiently doped, or if the absorber layer is depleted, a distinction between minority and majority carriers becomes difficult, and a more in-depth analysis may be needed, as discussed by Bube (1992).

The assumption of drift or diffusive transport is, of course, based on complete thermalisation within the absorber. This assumption appears to hold for most devices treated in this chapter with absorber thicknesses in excess of 100 Å. Taking a free carrier mobility of $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a thermalisation time of 1 ps and an electric field

of 10^4 V cm^{-1} , it is estimated that thermalisation will be accomplished within a distance of $100 \text{ \AA}$. Thus if the absorber is thicker than a few hundreds of Ångströms, thermalisation will be completed within the absorber layer. On the other hand, if thinner layers are used, carrier mobilities are high and strong fields are present, ballistic transport of hot carriers may occur. These conditions may hold in quantum-dot absorbers (Zaban *et al.*, 1998) and also in dye-sensitised cells (Moser *et al.*, 1999). This regime may offer some advantages for high-efficiency cells, particularly those based on quantum dots, as discussed in Chapter 3.

6.2.3 Band alignment

Thermalisation within the absorber imposes several constraints on the band alignment between the different layers. In Fig. 6.2b the band offsets between the absorber and the two transport layers are chosen such that thermalised majority-carrier injection into both transport layers is possible. Thus the conduction-band edge of the *n*-type transport layer is slightly ($\sim 0.3 \text{ eV}$) lower than that of the absorber layer, permitting electron injection into the *n*-layer. Hole injection at this interface is energetically not possible due to the large valence-band offset between the absorber and *p*-transport layer. Similarly, the valence-band alignment at the interface to the *p*-transport layer allows transfer of holes from the absorber into the *p*-type layer, while the conduction-band edge barrier at this interface suppresses the injection of electrons. When only majority carriers can be injected into the transport layers, the interfaces can be considered as blocking filters for minority carriers. This carrier filtering naturally supports carrier separation in the device (Würfel, 2005). When the transport layers are sufficiently doped, and only majority carriers are injected, transport is essentially recombination-free. In this case a simple analysis shows that large distances can be covered by the excess carriers. Hence under these conditions the transport layers can be comparably thick and need not be of very high electronic quality to ensure satisfactory charge collection.

6.2.4 Optical considerations

When the various layers of the device have different refractive indices and the structure feature size is in the region of the photon wavelength, there will necessarily be strong light scattering. In solar cells this is usually desirable, since it results in a longer optical path length (Green, 1981), as illustrated in Fig. 6.2d. In the strong-

scattering limit, the path enhancement may be quite substantial: for a material with refractive index n , the maximum path enhancement for a reflective back contact is $4n^2$ (Yablonovitch and Cody, 1982). Optical scattering may therefore allow a further reduction of the absorber thickness. Since this thickness reduction is accompanied by an increase in the carrier density in the absorber, it will also lead to an increased voltage and conversion efficiency (Würfel, 2002). A second advantage of a non-planar device therefore relates to its optical properties and results from an enlarged optical path arising from scattering. It can be expected that scattering will improve the absorptance of any structure patterned on the micrometre scale. Thus to harvest the potential advantages of both, a shorter transport path and an enhanced optical path, the scale of the structuring should encompass the nanometre and micrometre regime.

Summarising all points, the requirements for small transport distances, long optical paths, large junction fields and energetic carrier-type filtering suggest that a non-planar heterojunction design may bring about a number of advantages for transport-limited materials. The first cells of this type were explored with amorphous Si as an absorber by Wahi and Könenkamp (1993) and with amorphous Se by Tennakone *et al.* (1985). Polycrystalline cells have also been fabricated, such as a CdTe cell by Ernst *et al.* (2000, 2003), a CuInS₂ cell by Kaiser *et al.* (2001), a FeS₂ cell by Ennaoui *et al.* (1992) and an In₂S₃ cell by Hara *et al.* (2000). Even if a practical device may still lie far ahead on the photovoltaic road map, we believe that the exploration of the extended junction concept for inorganic semiconductors will produce useful and viable insights.

6.2.5 Overall quantitative description

While there exists a reasonable qualitative understanding to describe and optimise separate aspects of ETA cells, a more integrative and theory-based approach towards a quantitative analysis and towards an optimum design of these cells still appears rather difficult. This is because the geometry which is so easily achieved experimentally is not easily incorporated into conventional simulation programmes: while, on the large scale, ETA cells are planar, they are clearly three-dimensional on the small scale. What is worse, their micro-structure is irregular over a broad length scale reaching from a few nanometres to a few micrometres; and interface properties play a decisive role in both, the electronic transport and the optical properties. There have been two noteworthy attempts to obtain a theoretical description of this cell type, one by Burgelman and Grasso (2002) and the other by Taretto and Rau (2004). The work of Burgelman has focussed strongly on a realistic and simple interpretation of

experimental results from the CdTe-based ETA cell. The work of Taretto and Rau has addressed the ETA cell concept from a more general viewpoint and obtained estimates on the performance limits of these cells. Based on their work, conversion efficiencies of 15% appear possible—even with diffusion lengths as low as 10 nm.

6.3 Preparation of substrates, absorber and transporting layers

The unique geometrical structure of this type of solar cell imposes several challenges on the materials and the material processing. Despite progress in nano- and micro-patterning of thin films (Shalaev and Moskovits, 1997), there has so far been only very limited experience in applying these patterning techniques for solid-state devices to very large areas. Lithographic imaging and scanning methods appear to have only limited potential for photovoltaic applications. There is, however, a growing field of random and self-organising patterning techniques (Liz-Marzan and Norris, 2001) that would lend themselves more naturally to large-area applications. Some of these processing techniques are based on inexpensive gas- and solution-phase deposition. In this section we will discuss a few examples that promise to be scalable and cost-effective. We will also discuss possibilities of pattern transfer and manipulation on the nano- and micrometre-scale.

Beyond the fabrication of a patterned substrate there remains the need to prepare conformal and void-filling layers on these substrates. Recently, several solution and gas-phase techniques have been developed which allow conformal or void-filling deposition in very deep and narrow structures, and we will next outline how these techniques can be adapted for solar cell fabrication.

6.3.1 Substrates

Porous materials with large internal surface areas have attracted considerable attention in surface chemistry, catalysis and chromatography. In principle, a vast choice of porous materials is available. While some inspiration can indeed be drawn from chemical applications, the choices for useful photovoltaic substrate materials are considerably narrowed by the requirement to have thin-film constituency, transparency and electronic conductivity. Indeed, these requirements are so stringent that only a few substrate types and materials have so far been found suitable. Sintered nanocrystalline oxide films are one major class of these. Much development work on these materials has been reported in the context of dye-sensitised cells, and this is

covered in Chapter 8. We shall therefore restrict ourselves here to pointing out some important references. Oxide compounds such as ZnO (Redmond *et al.*, 1994; Keis *et al.*, 1999; O'Regan *et al.*, 2001; Vayssieres *et al.*, 2001) and TiO_2 (Barbe *et al.*, 1997) have been extensively used as *n*-type transport layers. SnO_2 has been explored by Bedja *et al.* (1994), Ferrere *et al.* (1997) and Tennakone (2001), while Nb_2O_5 has been investigated by Sayama *et al.* (1998) and Guo *et al.* (1999), and SrTiO_3 by El Zayat *et al.* (1998) and Burnside *et al.* (1999). CeO_2 has been used by Turkovic *et al.* (1997). Multilayer combinations of all materials are now under investigation in the development of dye-sensitised solar cells, and have produced very encouraging results, as reported in Chapter 8.

Chalcogenide compounds (Olea and Sebastian, 1998) and Cu compounds such as CuI (Rost, 1999), CuSCN (Engelhardt and Könenkamp, 2001) and CuAlO_2 (Kawazoe *et al.*, 1997; Tsuboi *et al.*, 2003) have been suggested and explored, the Cu compounds as *p*-type substrates.

Several different preparation and processing methods have been studied, including sol-gel techniques (Nazeeruddin *et al.*, 1993; Lindstrom *et al.*, 1996), spray pyrolysis (O'Regan *et al.*, 1996; Ernst, 2001), sintering of nanocrystalline powders, thermal and microwave treatment (Vigil *et al.*, 2000), oxidation (Zuruzi *et al.*, 2005), and electrochemical conversion (Pauporte *et al.*, 1999; Karupuchamy *et al.*, 2002). These methods mostly produce isotropic porous films, but there are also reports of columnar topologies and non-isotropic pore geometries (Pauporte *et al.*, 2003). Typically the films consist of single-crystalline grains with diameters between 1 and 100 nm. Sintering at moderate temperatures results in a structural connection between these grains, such that loosely packed but continuous films with large void fractions are obtained.

When the grains are sufficiently small and the sintering has produced only point-like melting necks, electron confinement effects can be observed (Könenkamp, 1996). In larger grain films with more extended connectivity, bulk electronic and optical properties become more prominent. However, low carrier mobilities due to the presence of surface and interface states, band-tail-like features in the absorption spectra and strong optical scattering at the grain/void interfaces remain typical in these films (Könenkamp, 2000a). Although a change of conductivity can often be induced by impurity doping, it is generally observed that the doping efficiency in nanocrystalline materials is very low. This is mostly due to a non-substitutional placement of the impurities: in very small crystallites there appears to be sufficient structural flexibility to accommodate impurities in their natural bonding structure, precluding substitutional inclusion in the host lattice and the delocalisation of excess carriers. Thus, Nb, when used as a dopant in TiO_2 , has the tendency to form a Nb_2O_5

environment instead of substitutionally replacing Ti in the TiO_2 lattice. A second effect relates to the large surface-state density in the porous films. These surface states act as traps for excess carriers and often induce strong Fermi-level pinning. Impurity-induced conductance changes are therefore often much smaller than expected. In fact, in many ‘doped’ nanoporous films, the observed conductivity is found to be due to a hopping-type defect conduction mechanism, and may therefore be of only limited use in devices. Figure 6.3a shows electron micrographs of porous nanocrystalline anatase TiO_2 films with a grain size of approximately 10 nm. The volume fraction in these films is about 50% and measurements by the BET method show that the internal surface area is several hundred times the planar area for a 5 μm thick film. Figure 6.3b shows a detailed micrograph of the interface area, indicating that there is indeed very little amorphous tissue between the grains. The films were prepared by spreading a colloidal solution over a glass substrate and subsequent annealing at moderate temperatures. This procedure results in very smooth film surfaces which do not give rise to any noticeable optical scattering. Figure 6.3c shows that the morphology can be varied by changing the processing conditions. Spray pyrolysis using heated precursor solutions and employing heated substrates results in films with essentially the same nanostructure as shown in Figs. 6.3a and b, but with a rougher surface morphology that gives rise to very strong optical scattering. This peculiar morphology in the sprayed films is due to fast evaporation in a short boiling period as the sprayed droplets impact on the heated substrate (Ernst, 2001). Both methods, spraying and grafting, are commonly used and several elaborate procedures have been developed to optimise structural, optical and electrical properties of the films (Grätzel, 2000).

Tennakone *et al.* (2002) have pointed out that the interface properties of many porous oxide films improve when a second wide-gap oxide is deposited on top of the nanoporous material. Typically Al_2O_3 or other oxides such as MnO with an average thickness of ~ 2 nm are deposited conformally from liquid solutions in the porous substrate. The favourable electronic effects of this coating have been confirmed for dye-sensitised cells (Tennakone *et al.*, 2001; Kay, 2002). While the physical origin of the effect is still under discussion, the obtained results indicate a decreased interfacial recombination rate (Palomares, 2003). The coating strategy has been particularly successful in liquid-junction dye cells, where the conversion efficiency can be more than doubled. Somewhat improved photovoltaic parameters have also been noted in solid-junction cells. An analysis of this improvement has been given by Grasso and Burgelman (2004).

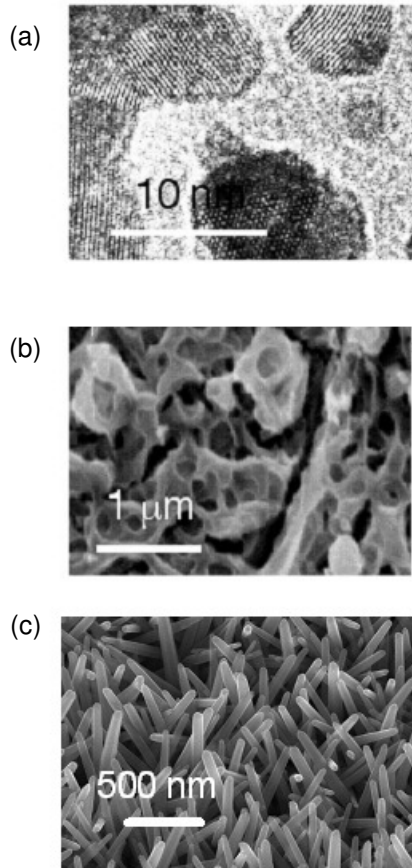


Figure 6.3 (a) Transmission electron micrograph of nanoporous TiO_2 film with 10 nm grains and ~50% volume filling; (b) Scanning electron micrograph of microporous TiO_2 . These films have a similar nanostructure to those shown in (a), but there is an additional microstructure caused by the spraying process; (c) Scanning electron micrograph of free-standing monocrystalline ZnO columns grown on a polycrystalline SnO_2 substrate.

From the experimental results it appears that electron transport in nanoporous films is strongly affected by grain boundaries. If the porous structure has a depth of $5\text{ }\mu\text{m}$ and the typical grain size is 10 nm, a minimum of 500 grain boundaries have to be crossed in the transport vertical to the film plane. It may therefore be worthwhile to consider alternative surface-enhanced substrates, which feature fewer grain boundaries, or those where these are completely avoided. There are essentially two possibilities for such films: porous structures etched in multicrystalline films, or grown columnar films with single-crystalline columns.

Si (Canham, 1990), SiC (Shor *et al.*, 1993), GaP (Belogorokhov *et al.*, 1994) and ZnTe (Zenia *et al.*, 1999) may be taken as examples of etched single-crystalline porous structures. Solar cells have indeed been fabricated with some of these materials, but it appears that the final product is as costly as the original multicrystalline precursors, and the cost advantages may therefore be limited.

Single-crystalline columnar growth may be the most promising technique for obtaining a sizeable surface enlargement with no grain boundaries along the transport path. Nanowire and nanorod formation have been demonstrated for many II–VI and III–V compound materials. The growth mechanism can often be understood as a minimisation of the polarised surface area. Figure 6.4 is a high resolution TEM micrograph for ZnO nanorods grown in electrodeposition at 90 C, showing that the columns are monocrystalline and the growth direction is along the hexagonal axis.

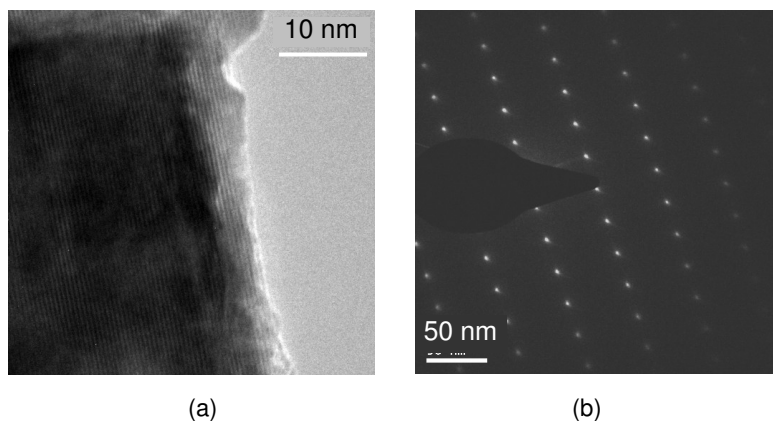


Figure 6.4 (a) High-resolution transmission micrograph of a single ZnO nanorod grown in electrodeposition; (b) Selected area electron diffractogram of a single ZnO nanowire with the *c*-axis perpendicular to the electron beam. The diffractogram indicates that the wires grow as single crystals.

Template-based growth techniques are another alternative for the preparation of columnar morphologies. Figure 6.5 shows CuSCN columns grown in ion-track-etched polymer films using electrodeposition. The polymer films were first exposed to a fast heavy-ion beam (400 MeV Ar) from an accelerator source. The passage of the ions through the polymer leaves a damaged track region which has a much reduced etch stability. In the case shown here these ion tracks were etched to a diameter of 100nm and subsequently filled with CuSCN by electrodeposition.

After dissolving the polymer foil, polycrystalline free-standing CuSCN columns with very large aspect ratios remain. Both freestanding and embedded columns can be used for device applications. The PET foils are an inexpensive large-area substrate, and the heavy ion exposure can be carried out in a fast non-vacuum process at a rate of approximately $1 \text{ m}^2 \text{ s}^{-1}$. As a large density of tracks can easily be achieved, the template growth process has some potential for the fabrication of flexible device structures (Engelhardt and Könenkamp, 2001; Chen and Könenkamp, 2003) and potentially for solar cells.

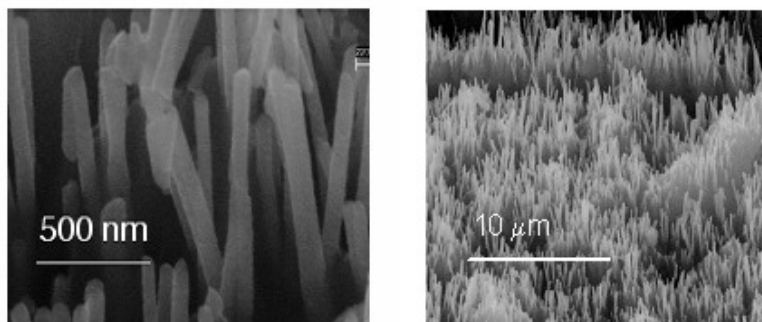


Figure 6.5 *p*-type CuSCN nanowires grown in polymer foil templates prepared by ion track etching.

6.3.2 Transfer of nanostructures and manipulation of the morphology

In many cases, growth method, material properties and processing are linked in an intricate way when a particular morphology is to be prepared. Often certain nanostructures can only be prepared for one particular material, or by only one growth method. This often imposes strong limitations on the material choice and the overall device design. It would therefore be desirable to have the capability to transfer a unique morphology from one material where it is easily obtained to another that is more suitable for a specific application. On the nanoscale this goal can be achieved by

using diffusive ion-exchange mechanisms that can be applied from the gas phase or from solutions. Starting with a film of vertically oriented monocrystalline ZnO columns, Dloczik *et al.* (2001) showed that the oxygen component in the ZnO crystallites can be readily replaced by S, resulting in a ZnS film with a very similar morphology to that of the original ZnO film. A second exchange step can then be applied to replace the Zn^{2+} ion by another metal ion, as for example Ag, Cu, Sb or Bi (Dloczik *et al.*, 2003). The two exchange processes combined result in films of Ag_2S_3 , CuS, Bi_2S_3 , or Sb_2S_3 with columnar morphology that bears a very high similarity to that of the initial ZnO films. Clearly, due to the limited diffusion lengths this exchange process is restricted to small scales, but it appears that for sub-micron dimensions a complete replacement of a given material is possible on reasonable time scales and at comparably low temperatures. Typically temperatures of around 400 °C were used, requiring processing times between 30 minutes and several hours. While the product materials may have quite different properties from the starting material, the morphology is largely preserved.

In some cases the kinetics of the exchange process can be sufficiently well controlled to allow only a partial exchange, and thereby produce a manipulation of the morphology. Since the conversion process proceeds from the periphery of the ZnO columns inwards, it is possible to restrict the conversion to the surface near region. Thus for the case of the ZnO-to-ZnS conversion, the solid ZnO columns can be converted to a hybrid structure consisting of a ZnO core and a ZnS shell. As the etching stabilities of ZnS and ZnO are quite different, the ZnO cores can subsequently be removed from the columns and free-standing hexagonal ZnS tubes can be prepared. As shown in the lower part of Fig. 6.6a, the wall thickness can be as low as a few nanometres. These partial conversions have mostly been carried out with H_2S vapours using accurate control of reaction temperature and duration. Naturally, the same principle can be applied to convert any other geometric structures from a solid to a hollow morphology. Thus the near-spherical crystallites in nanoporous materials could in principle be converted to foam-like structures with very large surface areas.

Complete conversion of the ZnO columns to ZnS columns has mostly been carried out in sulphur vapour. X-ray diffraction shows that the newly formed ZnS is in the zincblende phase, which is the stable phase at room temperature. From a detailed comparison of micrographs it was concluded that the ZnS column volume is measurably larger than that of the ZnO columns. This change in size was attributed to a different size and geometry of the ZnO and ZnS unit cells (Dloczik *et al.*, 2003).

For the exchange of metal ions in the newly obtained ZnS structures the ZnS films were immersed in aqueous solutions containing salts of Ag, Cu, Sb and Bi. The salts were chosen such that the valence state of the metal ion is the same in the solution as

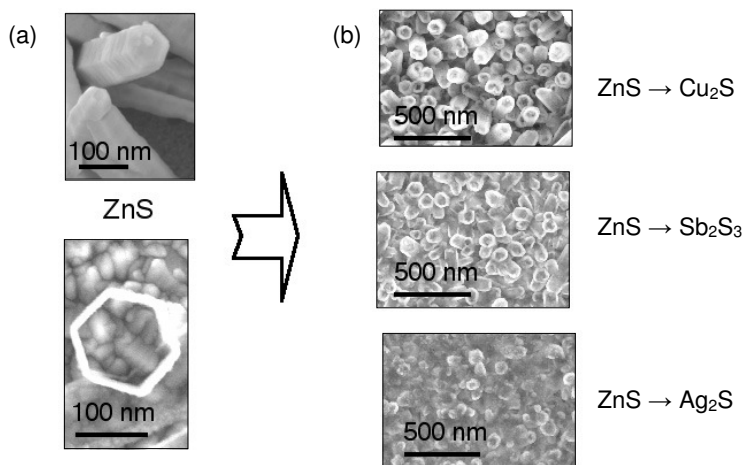


Figure 6.6 (a) ZnS columns and tubes obtained from single-crystalline ZnO columns by oxygen/sulphur ion exchange in the gas phase; (b) Tubular Cu_2S , Sb_2S_3 and Ag_2S obtained by metal ion exchange (metastasis) from solutions.

it is in the envisioned solid. For example, for the case of Cu_2S , the Cu valence is 1, and accordingly an aqueous solution of cuprous acetate, which has the same Cu valence state, is chosen to perform the ion exchange. For the preparation of Bi_2S_3 columns, in which Bi has a valence of 3, $\text{Bi}(\text{NO}_3)_3$ in H_2O was taken as the chemical precursor. Another aspect in the selection of the chemical solution is, of course, the solubility of the initial and the desired final compound. It is clear that, for a stable synthesis, the final compound should be at least as stable as the initial one. Dłoczik *et al.* (2003) have provided a detailed list and description of their solutions. Figure 6.6b shows the set of Cu_2S , Ag_2S and Bi_2S_3 films obtained from a ZnO precursor. In all of these cases the final morphology, which is either tube-like or columnar, is determined by the ZnS intermediate. Within the accuracy of X-ray diffraction measurements ($\sim 1\%$), the final compounds are pure and single-phase, as shown in Fig. 6.7.

6.3.3 Semiconductor deposition on deeply structured substrates

The deposition of absorber and contacting layers on top of deeply structured substrates requires working in a regime of highly conformal growth. It appears advantageous to select deposition methods in which the precursor constituents have small mean free paths, sufficient bulk diffusivity and a reasonable surface mobility.

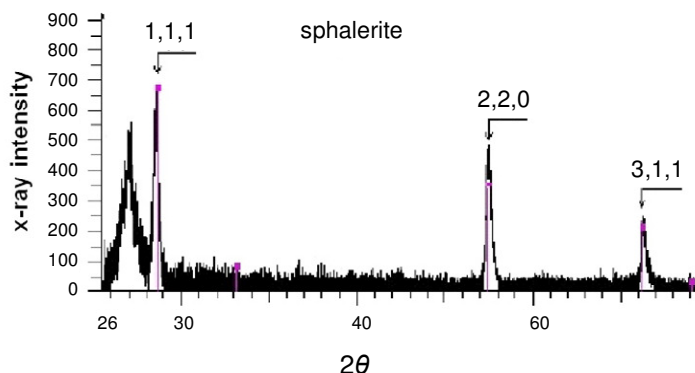


Figure 6.7 X-ray diffractogram of columnar ZnS films obtained after O $\rightarrow$ S ion exchange, showing that only the sphalerite structure is obtained.

These conditions will ensure that sufficient flux is maintained into deep narrow volumes, that shadowing and depletion effects during deposition are minimised and that a continuous conformal coverage is obtained. There are now several solution-phase deposition techniques available that show excellent surface coverage and a few gas-phase techniques that seem similarly suitable.

For compound semiconductors, one of the simplest approaches involves the monolayer adsorption of metal salts from liquid solutions, and a subsequent conversion of the salt to the desired semiconductor. This second step can be carried out in solution or in the gas phase.

The two processes are known as SILAR (successive ion layer adsorption and reaction) and ILGAR (ion layer gas reaction). Both methods work best when a metal salt is chosen in which the metal ion has the same valence state as in the desired final compound. Depending on concentration, temperature and duration, the thickness of the deposited metal can be varied from approximately monolayer thickness to more continuous single- or multi-layer coverage.

When the compound formation is performed from solution, the reaction product appears to obtain some mobility in the solution, and clustering is often observed. This clustering can be desirable when quantum dot growth is envisioned. As an example, Fig. 6.8 shows PbS quantum dots on the surface of nanoporous TiO₂, which were grown by adsorbing lead acetate from aqueous solution on the inner surfaces of a nanoporous TiO₂ film. After adsorption the Pb²⁺ ions were subsequently converted to PbS by exposure to a Na₂S solution. It is seen from the figure that the resulting PbS

crystallites are in the quantum-dot size regime. They show strong electron confinement effects in their optical and electronic spectra. Vogel *et al.* (1994) have explored this growth method for a variety of reaction paths and for the preparation of more complicated geometries, such as shell-like heterostructures and ordered quantum dot arrangements (Talapin, 2001).

When the compound formation step is performed in the gas phase, as in ILGAR, the end product is less mobile and therefore more homogeneously distributed over the surface. Very thin continuous layers can therefore be prepared in this way, as shown by Muffler *et al.* (2002). In their work one or more metallic components are deposited from solution on the substrate and then converted to the semiconductor compound by exposure to a reactant gas. The method is able to produce extremely thin coatings of chalcopyrite, chalcogenide and oxide semiconductors on nearly arbitrarily shaped substrates, including very deep nanoporous structures. A number of binary and ternary compounds, such as CdS, ZnS, CuInS₂, In₂Se₃, ZnO, ZrO₂, In₂O₃ and others, have been prepared.

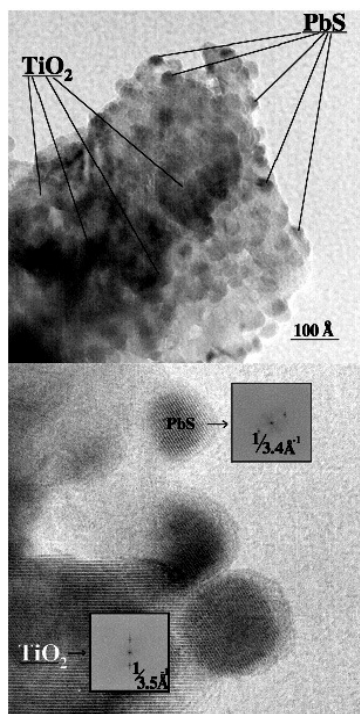


Figure 6.8 Transmission electron micrograph of PbS quantum dots in nanoporous TiO₂.
(Courtesy Dr. M. Giersig, HML.)

Figure 6.9 illustrates the capability to deposit thin layers in very deep structures. The figure shows an EDX line scan across a 4 μm thick nanoporous TiO_2 film whose internal surface has been coated by CuInS_2 using the ILGAR method. CuCl and InCl_3 were used as precursors in solution and H_2S as the reactant gas. The data indicate a homogeneous deposition of the ternary compound in the nanoporous network. X-ray diffraction shows that the predominant phase is roquesite, as in conventional CuInS_2 solar cells. Only at the interface to the SnO_2 -coated substrate there appears an excess of sulphur, which is attributed to a partial sulphurisation of the SnO_2 layer. Typically a single-cycle coating produces a layer thickness of 20 Å. Thicker layers can be prepared by repeating the procedure. If only a small number of coatings are carried out, the layers may not always be continuous. SEM and TEM work shows that the crystallite size can be in the quantum dot regime, and marked quantum confinement effects can be observed in the optical spectra.

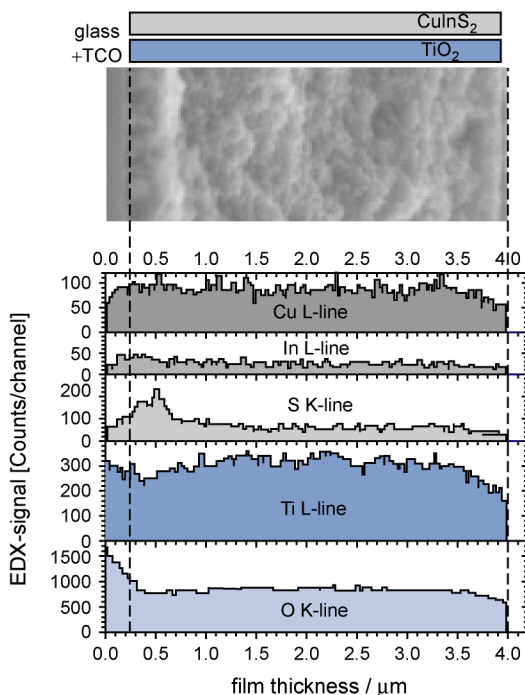


Figure 6.9 EDX (energy-dispersive X-ray emission) line scan across the cross-section of a nanoporous TiO_2 film filled with CuInS_2 in an ILGAR process. ILGAR has the capability to provide conformal coverage even in very small volumes at large depths.

An interesting alternative to purely chemical conversion methods is electrodeposition, which also allows conformal coatings to be obtained. So far, however, only somewhat shallower structures have been coated truly conformally, while deep structures, such as those of nanoporous films, are usually only coated close to the top surface. Figure 6.10 shows a thin CdTe layer deposited on a microporous TiO_2 substrate (Ernst *et al.*, 2003). As is apparent, some smoothing of surface features occurs in the deposition process.

Electrodeposition of CdTe uses solutions of CdSO_4 and TeO_2 at cathodic potentials in the range between -0.5 and -0.7 V vs. Pt reference. The deposition potential for the compound appears to lie midway between the deposition potentials of the metallic constituents, indicating that the formation energy for the solid contributes to the deposition process. This may foster the formation of a stoichiometric compound, as pointed out by Neumann-Spallart *et al.* (1990), but it also suppresses the surface selectivity. Since the compound forms in a single reaction step and not in a sequential process, it is possible that faster growth occurs in regions which are more easily accessible to the precursor solution. The faster deposition in these regions is, however, likely to prevent the penetration of precursor material into deeper lying regions. Therefore the deposited films have different appearance from those from the ILGAR method, and the penetration depth is considerably smaller.

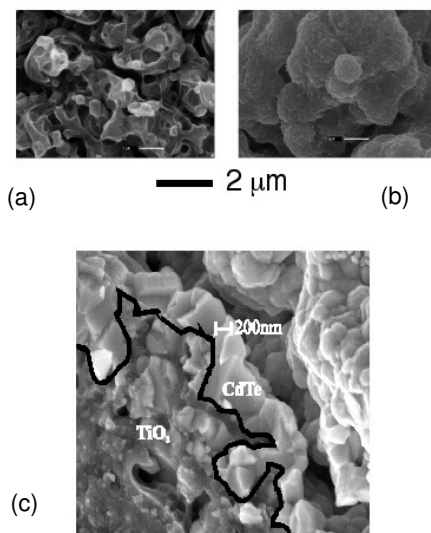


Figure 6.10 CdTe deposition on microporous TiO_2 . (a) Scanning electron micrograph of bare TiO_2 substrate; (b) TiO_2 substrate covered conformally by nanocrystalline CdTe; (c) Cross-section of the TiO_2/CdTe interface. A single grain layer is obtained in the electrodeposition.

There is, however, a specific advantage in the electrodeposition method, relating to the unique possibility of the determination of the amount of deposited material. For CdTe, the electrochemical reaction involves a charge turnover of six electrons for each deposited CdTe unit. This correlation is derived from basic chemistry, but it has also been experimentally confirmed by Ernst (2001), as shown in Fig. 6.11. This correlation holds for both planar and deeply structured substrates. Since the charge turnover can easily be measured by integrating the deposition current over time, the electrodeposition method affords a reliable and quantitative determination of the total amount of deposited material.

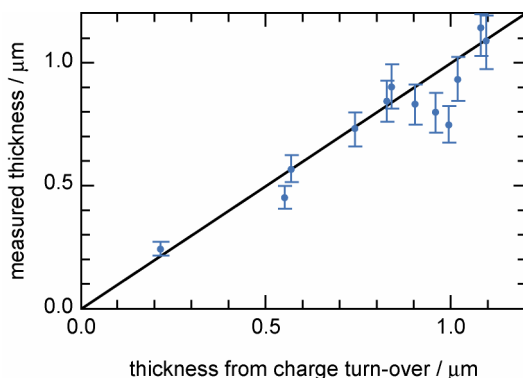


Figure 6.11 Thickness of electrodeposited CdTe layers determined by step-profiling and mass analysis vs. charge turnover obtained from integration over the deposition current (Ernst, 2001).

This determination is of key importance for the optical and electronic characterisation of solar cells, since a thickness determination is otherwise quite challenging. The as-grown electrodeposited CdTe is nanocrystalline and has rather poor electronic properties. Marked improvement is obtained in a subsequent annealing process involving CdCl_2 vapour and temperatures around 430 C, as described by Birkmire *et al.* (1991). If this process is performed in air, the crystallisation is accompanied by a type-conversion towards *p*-type material.

Several other approaches to thin-film deposition into porous materials from the liquid phase have been attempted, most notably the deposition of CuInSe_2 and CuInS_2 from colloidal solutions by Czekelius *et al.* (1999), and of InP by Zaban *et al.* (1998). Spray pyrolysis of CuInS_2 from liquid precursor solutions onto structured substrates has been explored by Krunks *et al.* (1999, 2001).

More recently, atomic layer deposition (ALD) has been pursued in deep nanostructures by Reijnen (2001) and Meester (2001). Gaseous metal-organic precursors

were used to deposit very thin films of CuInS_2 and FeS_2 in nanoporous titania. The deposition conditions and the precursors are chosen such that only one atomic layer is deposited per reaction cycle. Thus in the deposition of CuInS_2 , In is transported first as InCl_3 vapour to the substrate. The duration of the gas phase exposure is adjusted so that a sufficient degree of coverage and sufficient penetration into the porous network is obtained. After a purging step, exposure to gaseous CuCl occurs, resulting in a deposition of Cu preferably on In-covered surfaces, less on the TiO_2 . The In/Cu layer is subsequently reacted to CuInS_2 by exposure to H_2S . First experiments with ALD on nanoporous substrates indicate that the penetration rates for the different reactant gases are quite different, and that gas pulse durations and temperatures have to be finely tuned to produce a homogeneous stoichiometry in deep morphologies. For a depth of approximately $2\text{ }\mu\text{m}$, ALD can produce continuous coverage on the internal surface of titania, but the growth rates in this process are very low, rarely exceeding a few $\text{\AA s}^{-1}$.

Finally, plasma-assisted CVD processes have also been shown to have some potential for conformal coverage in unobstructed structures like trenches and grooves (Tsai *et al.*, 1986) and on columns. The conformality of the deposition is enhanced when the process is run under ‘chemical’ conditions with high pressures and low plasma energies, while the conformality is considerably reduced at low pressures because of the longer mean free paths and higher particle energies. We found that

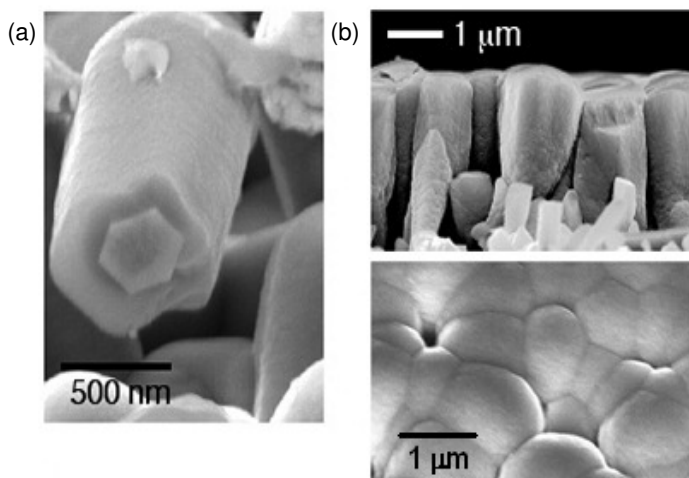


Figure 6.12 (a) Amorphous Si (a-Si:H) on single-crystalline ZnO. The a-Si:H is deposited in plasma-assisted chemical vapour deposition at 13.56 MHz; (b) Microcrystalline Si deposited by the hot-wire technique on columnar ZnO films.

amorphous and microcrystalline Si can be deposited conformally onto columnar ZnO substrates in plasma-assisted CVD and in the thermocatalytic hot-wire process. Some results are shown in Fig. 6.12 (Könenkamp, 2000b and 2001). Microcrystalline Si, however, shows a much smaller tendency for conformality and connectivity, as indicated in Fig. 6.12b.

6.3.4 Void-filling growth

As discussed above, a void-filling process is desirable to close the deeply-structured arrangement of the ETA cell and allow the deposition of a planar top or back contact. Presently, there appears to be very little work that provides guidelines for the selection of a suitable deposition method, and only one growth method for inorganic material has been reported. After noting the conformal growth in electrodeposition it may be surprising to find that the same method can also be used to obtain void-filling deposition (Rost *et al.*, 1999).

Figure 6.13 illustrates this possibility with the electrodeposition growth of CuSCN in a 8 μm thick nanoporous TiO_2 film. The CuSCN deposition involves CuI and HSCN complexes in aqueous solution at cathodic potentials of -0.7 V to -0.9 V vs. a Pt reference. Growth is initiated at the SnO_2 electrode, visible at the bottom edge of

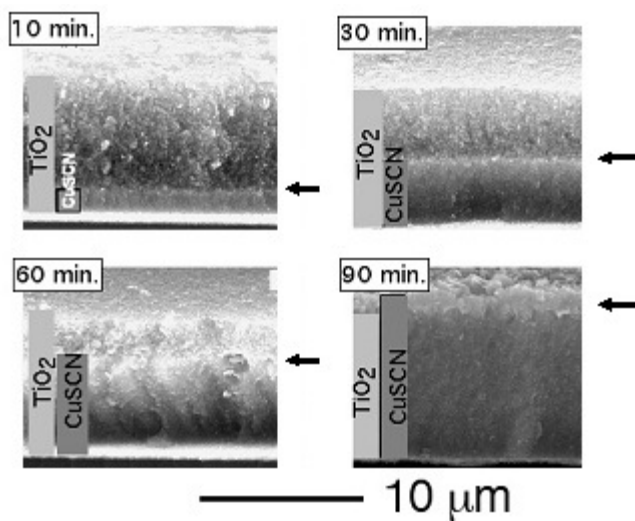


Figure 6.13 Electrodeposition of CuSCN in nanoporous TiO_2 film. The rectangular boxes indicate the deposition times; the arrows indicate the position of the growth front. The substrate electrode is located at the bottom of the micrographs. The TiO_2 film is $\sim 8 \mu\text{m}$ thick and has ~ 50 nm pores.

the micrographs, and proceeds upward through the nanoporous network, feeding from the solution of precursors through the network. The sequence of micrographs in Fig. 6.13 shows a coherent growth front progressing upward through the TiO_2 matrix, filling the void volume from bottom to top. After the growth front reaches the TiO_2 surface, the CuSCN connects to a continuous film and growth proceeds as a well-connected polycrystalline layer.

Gravimetry and volume determination indicate that the void volume in the TiO_2 is filled completely, with a possible 3% error due to limited experimental measuring accuracy (Rost *et al.*, 1999). After drying and annealing, the $\text{TiO}_2/\text{CuSCN}$ composite film constitutes a rectifying p - n heterojunction with a strongly enlarged interface area. Figure 6.14 shows the current–voltage characteristics of this junction.

We have for a long time considered the $\text{TiO}_2/\text{CuSCN}$ heterojunction device to be a frame structure for the ETA solar cell, since only the absorber layer is missing. Much of our work therefore focused on finding a suitable absorber, but chemical compatibility and processing characteristics have precluded a successful strategy so far. This issue will be discussed in more detail in Section 6.5.

While the void-filling characteristics of the deposition process are well documented in Fig. 6.13, the growth mechanism itself is not yet completely unravelled. It appears that in the case shown here the deposition threshold voltage is only reached at the CuSCN growth front, while the uncovered TiO_2 surface remains below threshold. As the deposited CuSCN is sufficiently conductive, the electrode potential moves with the growth front through the nanoporous volume, thereby producing a continuous void-filling deposition, while pushing the electrolyte out of the pore structure.

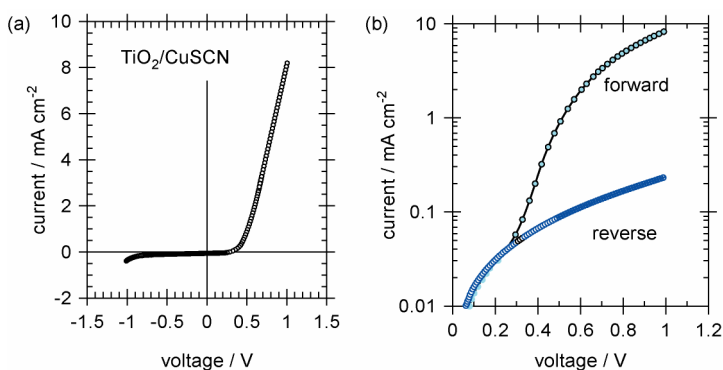


Figure 6.14 Current–voltage characteristics of an extended p - n junction between CuSCN and nanoporous TiO_2 : (a) linear scale; (b) logarithmic scale.

Only when a potential substantially larger than the deposition threshold is applied at the electrode will the deposition potential be attained on the TiO_2 surface or at the top of the TiO_2 layer, in which case a conformal coverage or top-surface deposition is obtained. Attempts to achieve void-filling coverage by electroless or purely chemical techniques have enjoyed only limited success. This is probably due to bottleneck effects in the transport path for the precursor solution as the deposition proceeds.

6.4 Electronic and optical aspects

6.4.1 Junction formation, band line-up and charge distribution

Planar semiconductor heterojunctions have been intensely studied over recent decades, and for many materials a detailed physical understanding of the interface structure and the resulting electrical and optical properties have been obtained. There remain, however, many open questions on the formation of *non-planar*, *non-epitaxial* or simply polycrystalline interfaces. The fabrication of these types of interface has therefore remained largely an empirical subject. The fundamental difficulties are the following: although for many materials there exist well-established data on electronic parameters such as the electron affinity, the ionisation energy and the Fermi-level position, these data appear to be of only limited practical value since they are growth-specific and refer to junctions to vacuum, inert electrolytes or to an epitaxial partner, and many practical devices do not satisfy these conditions. Post-deposition processes often result in transformations that strongly alter the electrical equilibrium, the band alignment, the Fermi-level position and the macroscopic charge distribution at practical interfaces. Furthermore, interfaces on polycrystalline materials usually involve more than one crystal plane, and therefore require a weighed average over different values to obtain the interface parameters. The dynamics of transport and recombination in the vicinity of interfaces add yet another element of complication since the transport and recombination dynamics strongly depend on the spatial arrangement and the electric field distribution. Considering these complexities, it is clear that an empirical approach is likely to give the most immediate and often the only reliable insight to practical situations.

In the following, some of the experiments that give rise to a qualitative understanding of a specific polycrystalline interface, that between CdTe and microporous TiO_2 , will be discussed. The band line-up at the CdTe/ TiO_2 interface has been studied using photoemission experiments, quantum efficiency measurements and numerical simulations based on a one-dimensional model of the $\text{SnO}_2/\text{TiO}_2/\text{CdTe}/\text{Au}$

heterostructure. Including data from electron microscopy, a first semiquantitative understanding of this structure has been obtained.

The photoemission work was carried out using planar films of TiO_2 on a $\text{SnO}_2/\text{glass}$ substrate, and depositing CdTe *in situ* in a thermal co-evaporation process. Valence band and core-level spectra were determined at different stages of the deposition. Due to their small scattering length, only electrons from an approximately 20 Å thick surface layer are emitted in the photoemission process. The photoemission spectrum carries information on the density of states near the surface, band bending, surface dipoles and photovoltage effects. By measuring the photoemission spectra at different stages of the CdTe growth process, it is possible to observe the development of band bending at the interface and to track the evolution of the valence-band offset at the junction. The band bending is best observed in the XPS spectra obtained from photoemitted core-level electrons. Figure 6.15a shows the $2p$ and $3d$ core levels of Ti and Cd, respectively, as CdTe is deposited in a low-rate co-evaporation process from Cd and Te sources. The CdTe thickness is given in monolayer equivalents. Shifts in energy and peak heights are observed as the CdTe coverage increases. The changes in the peak height reflect the decreasing emission probability from the TiO_2 substrate and the increasing emission from the CdTe as its thickness increases. The energy shifts indicate the emergence of band bending due to charge transfer and dipole formation at the TiO_2/CdTe interface. The Cd $3d$ level, split into the Cd $2+$ and Cd $3+$ oxidation states, is used to monitor the band bending in the deposited CdTe film, while the TiO_2 band bending is monitored with the Ti $2p$ peaks. Fitting the spectra with a combination of Lorentzian distributions allows the shifts in the peak positions to be tracked with high accuracy and the band bending to be established as shown in Fig. 6.15b (Ernst, 2001).

To determine the valence band offset at the heterojunction, one measures the onset of the photoemission spectrum at low electron-binding energies. This onset represents the valence-band edge at the sample surface. Before the deposition of the CdTe , one observes the valence-band edge of the TiO_2 , and as the deposition proceeds, the gradual development of the CdTe valence-band edge is seen. Using these data for the band bending one can calculate a valence-band offset of 2.6 V. Knowing the TiO_2 and CdTe bandgaps of 3.4 eV and 1.45 eV, respectively, the conduction-band offset is calculated to be 0.6 eV. This value is surprisingly large: based on published data for the CdTe and TiO_2 work functions and using the simple model due to Anderson (1962) for non-polar junction formation, a conduction-band offset of only 0.1 eV would be expected. The discrepancy is mainly due to the formation of a dipole layer at the TiO_2/CdTe interface, and to a lesser extent to the lower work function of the porous TiO_2 compared with the solid TiO_2 crystal. The interface dipole contribution

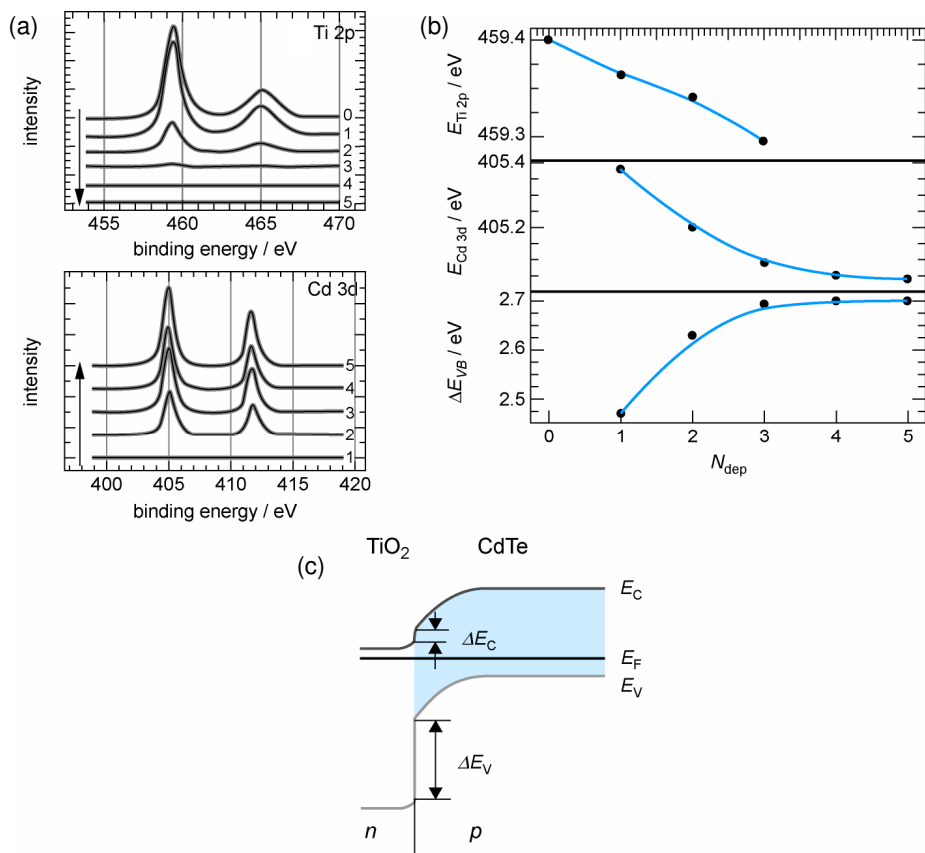


Figure 6.15 (a) Core-level spectra for the Ti 2p level (upper diagram) and the Cd 3d level (lower diagram) for various CdTe layer thicknesses. The numbers on the right relate to the estimated number of CdTe monolayers; (b) Binding energies as a function of CdTe overlayer thickness for the Ti 2p level and the Cd 3d level. The lower diagram shows the valence-band offset as a function of CdTe layer thickness. (Ernst, 2001); (c) Energy diagram showing the TiO₂/CdTe interface as determined from the XPS/UPS measurements. ΔE_c is the conduction-band offset, which is determined to be approximately 0.6 eV.

may have chemical or structural origin and is estimated to contribute ~ 0.4 eV to the measured band-offset value. The contribution from the TiO₂ work-function difference between porous and solid TiO₂ is probably due to a doping effect from photodesorbed oxygen, which would be much more prominent in the porous films.

It is in principle possible to determine the energy diagram for the whole heterojunction cell in this way. Indeed Mahrov *et al.* (2004) have recently carried out photo-

electron spectroscopy measurements on the *p*-type materials CuSCN and CuI, and studied the energy scheme for the coverage with a Ru dye layer. It is to be expected that the experimental method will soon give a complete analysis of a working device, which could then provide the basis for an accurate numerical simulation.

There are, however, several problems with this type of evaluation. One uncertainty relates to the photodesorption of oxygen during the photoemission experiments. This effect is well established for planar oxide surfaces, and it can be expected to be much larger for the case of nanocrystalline surfaces and interfaces (Könenkamp, 1996). Photodesorption will noticeably affect the work function at the surface, and thus the evaluation. Secondly, post-deposition treatment is used to change the crystallinity, doping and grain size in many of the practical devices. These post-deposition treatments cannot be characterised in the *in situ* photoemission measurements, since the experiment is so surface-sensitive and can effectively be performed only during the growth process.

Figure 6.15c summarises the data in a complete energy diagram for the TiO₂/CdTe interface. The value of 0.6 eV for the conduction-band offset is considered too high for efficient solar cell operation, since it results in a significant loss of energy when the electrons are transferred from the CdTe absorber to the TiO₂ transport layer. Previous work (Hoyer and Könenkamp, 1995) showed that 0.25–0.3 eV is sufficient as a driving force for carrier transfer and this value would be considered optimal in the ETA cell. On the other hand, the valence-band offset of 2.6 eV acts as an efficient barrier to hole injection from the CdTe to the TiO₂. This high barrier will strongly support carrier separation at this interface.

We now turn to considerations about the spatial potential distribution within nano- or micro-structured junctions. We consider four cases for the spatial arrangement of a *p–n* junction, starting with a simple planar case, then treating non-planar cases, as shown in Fig. 6.16. Figure 6.16a illustrates a simple planar *p–n* homojunction consisting of two doped transport layers. The junction geometry, charge distribution and potential profile are shown. To begin we assume that there is no absorber layer between the two transport layers. There will be some band bending towards the metallic contact layers adjacent to the two transport layers, but ideally the potential change at these interfaces will be small, if the characteristics are assumed ohmic, as is optimal for a solar cell. Most of the built-in potential can then be assumed to drop over the space-charge regions at the interface of the two transport layers.

When the doping in the two transport layers is due to shallow donors and acceptors, the charge distribution across the junction is as shown in the middle part of Fig. 6.16a. The electric-field profile and the potential profile can be obtained from Poisson's equation (Sze, 1981). For the planar case the depletion width w on each side

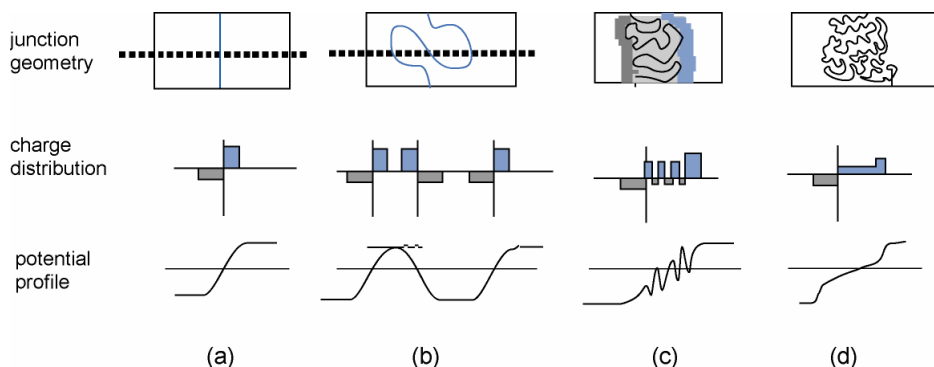


Figure 6.16 Junction geometry, space-charge profile and potential profile for an extended junction solar cell. (a) Planar junction; (b) Mildly curved junction with curvature radius larger than the space-charge width; (c) Curvature radius slightly smaller than the space-charge width; (d) Curvature radius much smaller than the space-charge width.

of the interface is approximately given by $w = [2\epsilon_s V_{bi}/(qN_B)]^{1/2}$ where V_{bi} is the built-in potential, ϵ_s is the static dielectric constant and N_B is the dopant density on either side of the junction. For a carrier density of 10^{18} cm^{-3} , $V_{bi} = 1 \text{ V}$ and $\epsilon_s = 10$, the depletion width is $\sim 50 \text{ nm}$.

To obtain a qualitative description of the non-planar case, it is useful to consider several limiting situations. We will characterise the non-planar case by a typical curvature radius in the junction plane and by a number n that gives the number of p - n junctions along a longitudinal cross-section through the junction, as indicated by the dashed lines in Figs. 6.16a and 6.16b. In Fig. 6.16b, the curvature radius is assumed to be approximately $1 \mu\text{m}$, and the number of junctions along the longitudinal line is $n = 3$. Since the curvature radius is well in excess of the space-charge width, the charge profile and potential profiles across each of these junctions is still qualitatively similar to those of the simple planar case. When we let n increase further and the curvature radius decrease, the geometry becomes more intertwined. As a consequence a larger portion of the semiconductor volume becomes depleted and the interface area increases. Eventually, when the curvature radius falls below the space-charge width, the depleted volume coalesces to a region that comprises all of the intertwined region. Starting at this point there will not be enough charge in the pockets of the junction to produce the full value of the built-in potential. Accordingly the potential variations will lose amplitude. This situation is indicated in Fig. 6.16c. If we again assume a carrier density of 10^{18} cm^{-3} , and then take the planar depletion width as a first-order estimate, we expect this volume depletion effect to set in for a curvature radius below

50 nm. Eventually, at even smaller curvature radii, another interesting effect sets in: since for a dopant density of 10^{18} cm^{-3} , the average distance between the dopant impurities is of the order of 10 nm, the dopant distribution will become coarser than the material interface. In other words, not every pocket has an impurity atom in its bulk or at its interface. Since the electric field is actually produced by the charged impurity atoms, there is no longer a correlation between the interface and the electric field, and accordingly, the electric field can no longer be expected to support charge separation at the interface. While large electric fields may still exist in the heterojunction volume, these fields no longer correlate with the heterojunction geometry, *i.e.* at this level the charge and field distribution is random and calls for a different description. The statistical evaluation of potential fluctuations arising from randomly distributed dopants carried out by Jäckle (1980) is quite useful in this context.

To summarise Jäckle's argument, it appears that a significant feature in the charge-collection process is lost at very small grain sizes. This loss of electric field support at the semiconductor/semiconductor interface may explain why solid ETA cells with very small feature sizes have not yet been found to produce the high efficiencies observed in micrometre-sized interface structures. Nonetheless, if there are energetic barriers at the interface, as for example in the form of large band offsets, one may still expect some charge separation due to these energetic driving forces. Similarly, entropic effects may remain effective in the charge separation, where different bands with largely different densities of states border each other: for example, in dye-sensitised solar cells the very large density of states in the solid drives the electron away from the dye molecule as a consequence of probability, *i.e.* entropy.

When the junction curvature radii are very small, one may view the dopants as homogeneously distributed. When the doping densities are equal under these conditions, essentially no macroscopic voltage drop occurs in the junction volume. If the doping densities of the *n*- and *p*-type layers are not equal, there remains a net charge in the junction region, as shown in Fig. 6.16d. This uncompensated net charge will give rise to a small potential drop across the junction. But if the total amount of uncompensated charge is small, the potential variation in the junction volume will also remain small and most of the potential change then necessarily occurs at the interfaces between the transport layers and the metallic contacts.

When a thin absorber layer is embedded between the transport layers, the main ingredients of this qualitative description can still be applied. Since the electric displacement vector across the interfaces is continuous and since the absorber layer is assumed thin and of low conductivity, it is clear that the absorber layer is subject to electric fields similar to the junction field. If the junction curvature is not too small,

this field will support the charge-separation process and promote the injection of excited carriers from the absorber into the transporting layers.

There are two more cases of interest relating to the ETA cell. For the first case we assume one transport layer to be metallic rather than semiconducting. This case relates to the structure shown in Fig. 6.2d. It also applies to the dye-sensitised cell where one transport layer is an electrolyte of high conductivity. The interface between the metallic transport layer and the absorber can then be considered to be an equipotential plane. If, in a first approximation, the absorber layer is assumed to have a doping density N , a local thickness d_a and static dielectric constant ϵ_a , the absorber will supply a screening charge Nd_a , which results in an electric field $\mathcal{E} = qNd_a/\epsilon_a$. Inserting typical values of $N = 10^{18} \text{ cm}^{-3}$ and $d_a = 30 \text{ nm}$, one finds the field to be $\mathcal{E} = 5 \times 10^3 \text{ V cm}^{-1}$. This is sufficient to exert a favourable effect on charge separation and transfer. Thus, as stated in Section 6.2, a metal contact that replaces the transparent transport layer may be a feasible first approach towards a non-planar cell design.

The second case is where both transport layers are transparent metallic conductors with a work function difference $\Delta\Phi$. If the metallic layers are separated by an extremely thin absorber of thickness d_a , the work function difference will be dropped nearly completely across the absorber layer. This will give rise to an electric field of strength $\mathcal{E} = \Delta\Phi/qd_a$. Clearly, if the semiconductor is sufficiently thin this field can also be quite large, and this configuration would therefore also produce a useful driving force for charge separation.

The main problem with the use of metallic layers in direct contact to the absorber lies in the large density of states near the Fermi energy in metals. The proximity of this large density of states opens a very effective recombination channel that often precludes a reasonable quantum efficiency. When the metal contacts are separated from the absorber by a transparent, majority-carrier transport layer, the recombination problem can be avoided and much better efficiencies can be expected.

6.4.2 Transport in nanostructured materials

It would be appropriate now to discuss charge transport in the different layers of the cell. However, experimental data on this topic have remained very scarce. Most work has focused on electronic transport in nanostructured films used for substrates, particularly TiO_2 and ZnO .

The present understanding of electron transport in these nanostructured oxides has improved significantly with the many detailed investigations in the electrolytic dye-sensitised solar cell. The accepted picture explains the surprisingly efficient electron

transport through the nanoporous TiO_2 to be a result of a favourable charge-screening effect mediated by the electrolyte (Zaban *et al.*, 1997). It is therefore a serious question, if one can expect similar electron-transport behaviour in solid-state devices, where this screening action may not be operative. A number of experimental results appear to indicate, however, that there is a strong similarity in the transport behaviour of TiO_2 in electrolytic and in solid or even gaseous environments.

There is considerably less work on very thin absorber layers, prepared with the methods that are typically used for the preparation of highly structured cells. We will present results from work on our CdTe films electrodeposited on TiO_2 . These results appear to indicate that the transport parameters in these nanocrystalline films are much inferior to those typically observed in polycrystalline films of micrometre thickness. Nonetheless, they may be sufficient for solar cell operation in non-planar arrangements.

At the end of this section we shall briefly discuss transport measurements on polycrystalline CuSCN and CuI films, which have been used as transparent *p*-type transport layers in some devices.

Transport in nanostructured transparent oxides

Electron transport in ‘dry’ nanoporous TiO_2 has been extensively studied by several groups, and it is now well accepted that the transport is dispersive (Könenkamp, 2000a) owing to a broad distribution of traps, which are thought to be due to surface- and interface-related structural defects. With the large surface area of nanoporous films, the electronic properties are also dependent on the ambient. Thus it has been established that the transport behaviour is quite different for N_2 and O_2 ambients, and that the transport properties change drastically under the influence of water vapour (Weidmann, 1998; Könenkamp, 1999). When the ambient is an electrolyte, polarity, redox potential and chemical adsorption appear to have a strong influence on the charge transport. The key to understanding these influences is the notion that surface effects, whether they are of chemical or physical origin, can give rise to a charge redistribution which extends quite deep into the grains, the characteristic distance being the Debye screening length (Rose, 1978). The screening length depends on the conductivity and can be of the order of 100 nm in TiO_2 . When the grain size is of this magnitude, and a sensible fraction of the grain surface is exposed to the ambient, then essentially all of the grain volume, and thus all of the porous film volume, is affected by surface effects.

These surface effects can change with the electronic occupation of the surface states. Since the energy distribution of surface states is usually broad, trap-filling

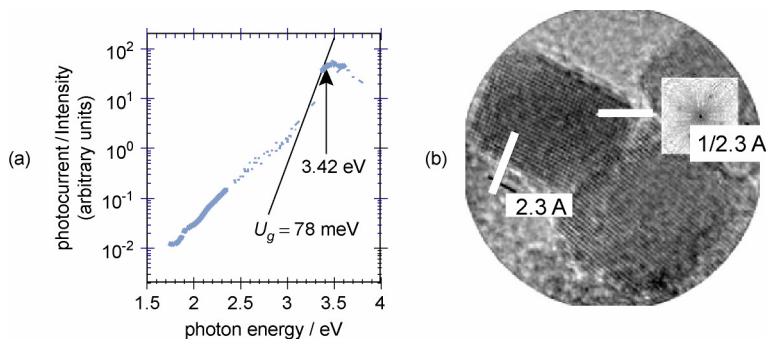


Figure 6.17 (a) Photoconductivity spectrum of nanoporous anatase TiO_2 film, showing broad defect distributions in the bandgap; (b) Transmission electron micrograph of sintered TiO_2 grains and spatial Fourier-transform spectrum indicating the lattice plane separation.

effects can be observed in the high- and low-injection regime and can have a sizeable influence on the recombination behaviour (Rose, 1978). Figure 6.17 shows the photoconductive response spectrum of a $\text{Pt/TiO}_2/\text{SnO}_2$ diode.

The photoconductivity extends deep into the midgap region, *i.e.* far below the bandgap energy, which is 3.42 eV for anatase (Tang, 1995). There are two exponential tail regions, with characteristic energies of 50 meV and 200 meV, in the sub-bandgap response. These tail regions can assume quite different shapes when the film is exposed to different ambients (Weidmann, 1998; Könenkamp, 1999). Figure 6.17b shows the crystallinity and interface structure of the TiO_2 grains in these films. It is apparent that the crystallites are monocrystalline, and that there is very little amorphous structure at the surfaces and interfaces in these films. We have used the junction-recovery technique (Könenkamp, 1999) to determine recombination lifetimes and carrier mobilities in films with defect distributions, as shown in Fig. 6.17a. In the junction-recovery technique, electrons and holes are injected from the two contacts under forward bias. The forward current in these diodes is predominantly due to recombination in the bulk of the diode.

The occupation of gap states can be varied over a large range, and high-injection conditions are easily studied when the bias voltage approaches the bandgap value. Figure 6.18 shows that, for a very large range of injection conditions, the mobility–lifetime product remains approximately constant, while the recombination lifetime is seen to decrease with injection, indicating that the ambipolar drift mobility increases with injection level. These results find a straightforward explanation in a simple trap-filling model: as the injection level increases, the localised states in the gap are filled to progressively higher energies, more and more occupied trap states participate in

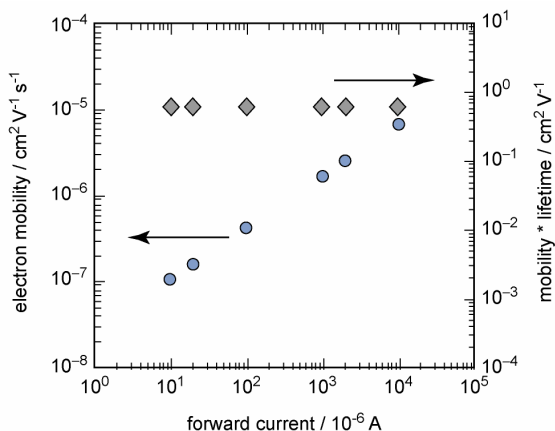


Figure 6.18 Results from junction-recovery measurements on $\text{SnO}_2/\text{TiO}_2/\text{Au}$ diodes. The electron drift mobility and the mobility–lifetime product are determined for various injection conditions and forward bias. The electron mobility is found to increase with increasing injection level, while the mobility–lifetime product remains approximately constant. These findings can be consistently explained in a transport model based on trap filling and a transport-limited recombination mechanism. An alternative explanation can, however, also be based on a tunnelling transport model (Könenkamp, 2000a).

recombination traffic, and the recombination time decreases. Concomitantly, as more localised states become occupied with injected carriers, there is a strong increase in the free carrier density. The drift mobility is defined as $u = (n_f/n_t - n_f)u_0$, where n_f and n_t are the free and trapped carrier densities and u_0 is the free carrier mobility. As the ratio n_f/n_t goes up, the drift mobility also increases. The mobility–lifetime product is experimentally found to remain approximately constant for both gaseous and electrolytic ambients, indicating that the recombination is transport-limited. A quantitative description of these findings for gaseous ambients has been given by Könenkamp (1999), and for electrolytic ambients by Peter and Wijayantha (1999).

When there is no hole injection, recombination cannot occur because there are no counter charges. Electron trap-filling may then result in improved transport conditions with higher mobilities and large carrier ranges. These are the conditions for which TiO_2 works well in solar cells. In the dye-sensitised cells it has been worked out that the electrolytic ambient favours a separation of electrons and holes at the $\text{TiO}_2/\text{electrolyte}$ interface. The fact that holes are not injected into the TiO_2 consistently explains the surprisingly good transport behaviour. In solid-state cells the extended junction may also lead to very effective charge separation, as we noted in the previous section, and this in turn may improve the transport conditions. Detailed experiments in support of this interpretation have not been carried out, however.

Since grain boundaries and interface defects appear to be responsible for the observed low carrier mobilities, other substrate morphologies may be more desirable for solid-state cells. In the single-crystalline columnar films shown in Fig. 6.19, carrier mobilities can be expected to be large and the transport may be non-dispersive. Using infrared reflectance measurements we were able to determine the transport properties in the ZnO columns. The experiments used a detailed numerical program to simulate the reflectance of the ZnO/SnO₂/glass layer structure in the region of the free-carrier plasma frequency. The free-carrier concentration and the free-carrier mobility can be obtained from these measurements. The table in Fig. 6.19 indicates that mobilities in the range of 10–20 cm² V⁻¹ s⁻¹ for carrier concentrations of the order of 10²⁰ cm⁻³ are typical. These values compare well with values obtained in

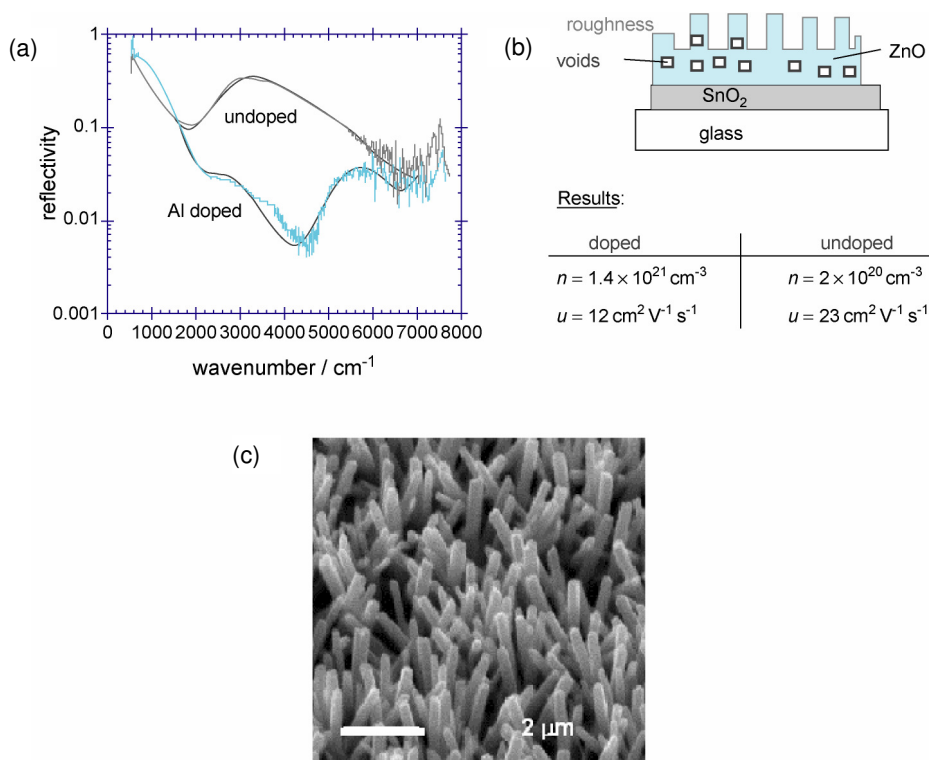


Figure 6.19 (a) Infrared reflectance data on undoped and Al-doped columnar ZnO films. Experimental data and a numerical fit based on the free-carrier response in a multilayer system are provided; (b) The numerical simulation treats the sample as a 3-layer system consisting of the glass substrate, the conductive SnO₂ contact and a structured ZnO film, with parameterised void-filling fraction and surface roughness, as indicated; (c) Scanning electron micrograph of a columnar ZnO film.

continuous polycrystalline thin films, and are much better than found in nanoporous TiO_2 . It is therefore believed that these columnar ZnO films hold great potential for photovoltaic applications. In essence, the monocrystalline columns can be considered as electron highways for the transport of photogenerated electrons from the absorber into the underlying contact.

There has been some work on the electrical characterisation of transparent *p*-type conductors, particularly CuI and CuSCN (Tennakone *et al.*, 1998a, b). However, the characterisation focused on continuous thin films rather than on structured layers. For CuSCN, Hall mobilities of the order of $20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been reported and similar values were found in CuI films (Rost, 1999), indicating that both materials are well-suited for device applications. So far, however, solar cells involving these materials with efficiencies beyond 3–4% have not been reported. Both materials, CuSCN and CuI, have rather high diffusion coefficients for Cu diffusion. These findings raise the question if stable devices can be fabricated, or if Cu migration and diffusion effects may render thin-film devices inherently instable.

Transport in extremely thin, non-planar, nanocrystalline absorber layers

Ernst (2001) has examined the minority-carrier transport in the CdTe/ TiO_2 /Au ETA cell in some detail. Based on the accurate thickness determination that is possible in the CdTe electrodeposition process, it was possible to estimate the minority-carrier diffusion length in the nanocrystalline CdTe material.

For a large sample number it was concluded that the electron diffusion length is approximately 130 nm in the annealed *p*-type material. This very low value is somewhat surprising since polycrystalline CdTe processed under similar conditions often shows diffusion lengths of over 1 μm . The much lower value found for the non-planar nanocrystalline films is probably due to interface recombination. Figure 6.20 shows the spectral collection efficiency in a CdTe-based ETA cell as a function of the applied bias voltage. Using a detailed model based on the combined effect of diffusion and field-assisted drift, the diffusion length is determined to be 130 nm from a least-squares fit to these experimental data.

To summarise these few experimental results, it can be stated that electronic transport in many nanostructured polycrystalline materials appears to be rather poor, particularly when the transport path involves grain boundaries. Yet in many cases the transport conditions can be improved by operating these films under majority-carrier transport conditions and exploiting trap filling under high-injection conditions. Efficient charge collection can then often be achieved. In absorber layers, where both carrier types are necessarily present, these conditions cannot usually be implemented.

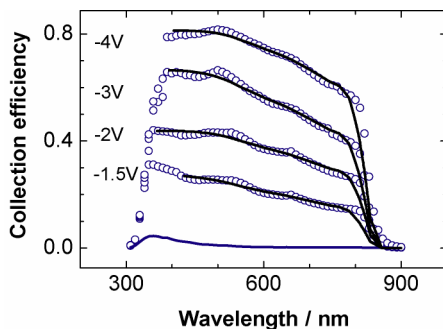


Figure 6.20 Spectral quantum collection efficiency in a CdTe /TiO₂ heterojunction cell for various bias voltages. The solid lines give a best fit to the experimental data, based on a minority-carrier diffusion length of 130 nm (Ernst, 2001).

If diffusion or drift lengths are low, the only way out is to change the layout of the cell in such a way that the local distance to the collecting contact falls within the possible transport path length. This guideline was followed in the CdTe-based ETA cell, where the local absorber thickness corresponded quite accurately to the estimated diffusion length.

6.4.3 Optical properties

It is well known that light trapping by randomisation of the optical path is a very efficient way to improve the operation and performance of solar cells. As noted by Yablonovitch and Cody (1982), the optical path in a non-absorbing light-trapping medium with a reflective back contact can be enhanced by the factor $4n^2$ where n is the refractive index. In the low-absorption limit, this corresponds to an enhancement of the absorptance by the same factor. Figure 6.21 shows the principle of light trapping in an infinitely extended film with a reflective back surface. Only light rays with angles δ from the normal smaller than the angle for total internal reflection will escape from the film. This is given by the condition $\beta = \arcsin(n_1/n_2)$, where n_1 and n_2 are the indices of refraction at the two sides of the interface. In our case $n_1 = 1$, since the interface is with air. The reduced escape angle leads to an increased energy density in the optical medium. When the scattering renders the light distribution in the film isotropic and the back plane is assumed to be reflective, the intensity is calculated to be a factor of $4n^2$ larger than the incident intensity.

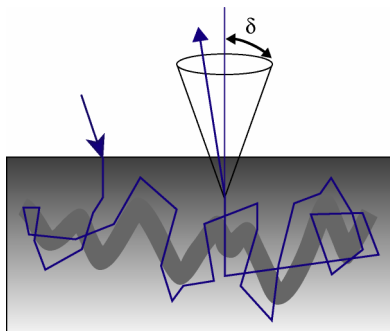


Figure 6.21 Illustration of light trapping in a solar cell with an embedded porous layer sequence. Light enters nearly vertically and is scattered at the layer interfaces. When reflective back contacts are assumed, only a small fraction of the scattered light within the cone δ from the normal can escape from the film. With an embedded absorber, light absorption in the region of small absorption coefficients is significantly enhanced.

Microporous films of TiO_2 , discussed in the context of Fig. 6.3b, can act as nearly ideal scatterers. Figure 6.22a compares the angular reflectance distribution for vertically incident green light for a microporous and a planar film surface. For the planar case the specular reflectance is approximately six orders of magnitude larger than the scattered background distribution, while for the microporous film the specular reflectance peak completely disappears and all of the reflectance is diffuse. The angular distribution closely matches a cosine distribution, as for an ideal Lambertian scatterer. These data show that a complete randomisation of directed light is possible in a thin-film arrangement. A more in-depth study by Wiersma *et al.* (1997) further indicates that thin-film arrangements can be used to induce weak photon-localisation effects. When an absorber is brought into the vicinity of a randomising structure, the absorption probability increases because of the extended optical path in the scattering medium. Figure 6.22b shows that a coating of CdTe reduces the integrated angular reflectivity further and thus leads to a significant increase in absorbance for photon energies between 2.4 eV and 1.5 eV.

Clearly, a single optical randomising layer could be integrated into a solar cell in several different ways: it could operate in transmission on the light-entry side of the cell or in reflectance at the back side of the solar cell. The morphology of this optical layer could also be independent of the morphology of the rest of the cell structure. Thus an optically rough layer could be deposited on top of or behind an otherwise planar cell structure and this configuration could still profit from randomisation effects. In the extended-junction cell it appears natural, however, to look for a more

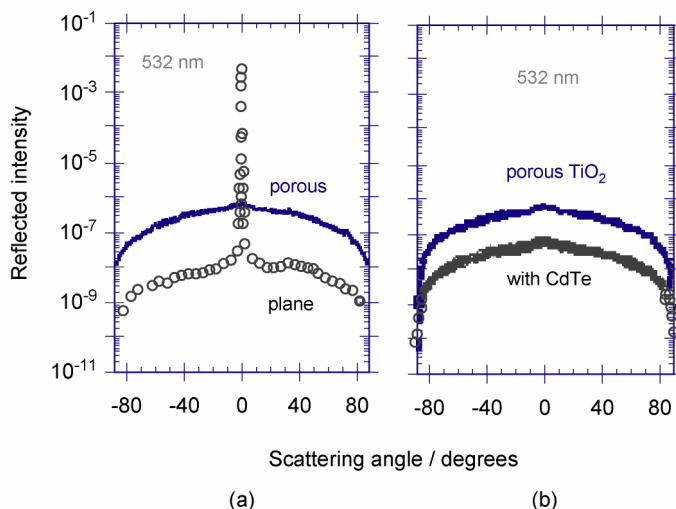


Figure 6.22 Angle dependence of the reflectance at a wavelength of 532 nm for various substrate and absorber configurations. (a) Planar and a microporous TiO₂ film on SnO₂/glass at vertical light incidence: the specular reflectance peak disappears in the microporous films and a cosine reflectance distribution with no specular feature is obtained; (b) When a thin CdTe film is deposited on the structured TiO₂, the overall reflectance is lowered owing to strong absorption in the CdTe.

integrative and synergetic approach between the optical and electrical functions, since the two envisioned effects, the implementation of a short transport path and a long optical path, both need geometric structure. Since a deep structure needs to be imposed on the absorber layer to reduce the transport length of excited carriers, there will necessarily be at least one rough interface. Practical designs will probably even produce two or more rough interfaces. These will make a quantitative optical analysis quite challenging.

The message from Fig. 6.21 in this context is that strong randomisation appears to be easily obtained even from thin transparent films, as long as the surface structure has some depth and the typical feature size covers the relevant wavelength region. While randomisation is readily obtained in transparent films, its effects become even more pronounced in absorbing films, because the probability of the light ray escaping is further reduced. Thus in the overall design of extended-junction cells it only needs to be ensured that the feature size of the absorber structure extends into and covers the wavelength region of sunlight. Figure 6.22 indicates that film morphologies which can easily be prepared satisfy these conditions and can provide for very strong randomisation effects.

A strong optical enhancement of absorption can also be obtained from columnar substrate morphologies. Figure 6.23 shows the optical properties of a microcrystalline Si:H film deposited on a columnar ZnO substrate. Near the Si absorption edge a strong gain in absorptance is observed. Evaluating these experimental data in terms of a light-scattering model, as proposed by Deckman *et al.* (1983), we find that the light-trapping efficiency reaches 70% of the maximal value of $4n^2$. The loss of 30% is mostly due to absorption in the TiO_2 and at the TiO_2/Si interface. It can thus be stated that columnar films also provide a strong optical scattering effect, although their surface enlargement is considerably smaller than that of porous films, and their effect on the electronic transport is therefore smaller.

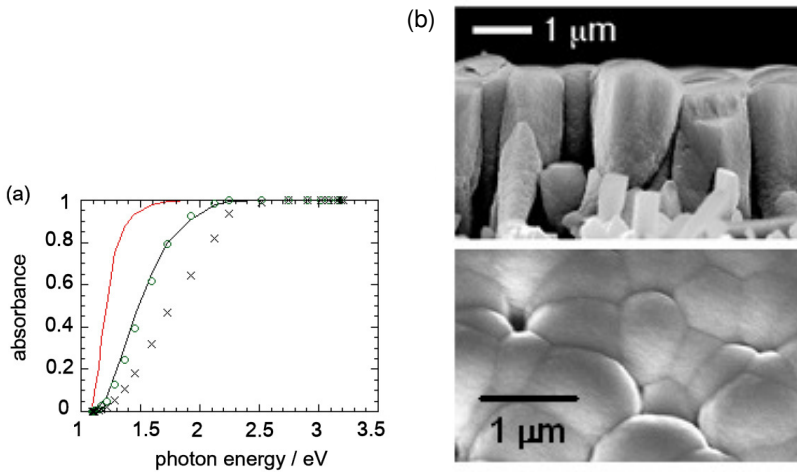


Figure 6.23 (a) Comparison of the absorbance of a 2 μm thick microcrystalline Si film. The solid line indicates the theoretical light-trapping limit based on a $4n^2$ path enhancement. The circles are experimental data obtained from a 2 μm thick film deposited on a columnar ZnO substrate, and the crosses are obtained for a 2 μm thick Si film on a planar substrate. The experimental data can be fitted with the known Si absorbance for a 2 μm thick film and a light-trapping efficiency of 70%; (b) Electron micrographs of microcrystalline Si layers grown on columnar ZnO nanorods. Upper micrograph: cross-sectional view, lower micrograph: view from above.

6.5 Devices

In this section we will discuss examples of the ETA solar cell based on porous TiO_2 substrates, with CuInS_2 , CdTe and quantum-dot PbS absorbers.

6.5.1 CuInS_2 -based solar cells

Early work attempted to draw a close analogy between the dye-sensitised cell and the ETA cell. Much of the experimental work therefore focused on nanoporous TiO_2 as the substrate material. For the deposition of a CuInS_2 absorber layer into the nanoporous network, several methods such as electrodeposition, spray pyrolysis and atomic layer deposition have been explored. Our own efforts have concentrated on combining the ILGAR technique and electrodeposition to prepare the structure glass/ SnO_2 /nanoporous TiO_2 / CuInS_2 /CuSCN/Au. Krunks *et al.* (1999, 2001) and Wienke *et al.* (2003) successfully used solution chemistry and spray pyrolysis to deposit CuInS_2 absorbers on TiO_2 , and Nanu *et al.* (2003, 2004) have applied atomic layer deposition for FeS_2 and CuInS_2 deposition in nanoporous TiO_2 .

As discussed above, ILGAR produces a fairly homogeneous coverage inside nanoporous TiO_2 substrates, one deposition cycle corresponding to an average local layer thickness of approximately 8 nm. Electrodeposition can then be applied to fill the remaining void volume with a transparent *p*-type transport layer of CuSCN, and in a subsequent step the structure can be coated with a reflective Al/Au back contact using vacuum evaporation. Figure 6.24 shows the quantum efficiency typically obtained for this type of cell for a variety of absorber layer thicknesses. The data indicate that sizeable photocurrents can only be drawn under quite strong reverse-bias conditions. Under short-circuit conditions the current densities remain below $1 \mu\text{A cm}^{-2}$. This behaviour may be due to a high series resistance across the device, a weak charge separation efficiency in the absorber layer, or inefficient transport in one of the various layers. Since cells with a thin absorber layer show higher collection efficiencies, it appears likely that charge separation in the absorber is a relevant problem, and that the thin CuInS_2 layer or its deposition process needs improvement.

Wienke *et al.* (2003) and Bayon *et al.* (2004) showed that substantial improvement in conversion efficiency is obtained when a thin indium hydroxysulphide ($\text{In}_x(\text{OH})_y\text{S}_z$) layer with a bandgap of approximately 2.5 eV is deposited prior to the CuInS_2 deposition. The observed improvement is attributed to a reduced hole density in the vicinity of the $\text{In}_x(\text{OH})_y\text{S}_z$ contact. The CuInS_2 was prepared in a spray pyrolysis process. Nanu *et al.* (2003, 2004) employed atomic-layer chemical vapour deposition to obtain ultra-thin CuInS_2 layers inside the pores of nanostructured TiO_2 . CuCl , InCl_3 and H_2S are used as precursors in this process. A growth rate of $1\text{--}3 \text{ \AA s}^{-1}$ is observed, and conversion efficiencies slightly above 4% have been obtained. While the process may not be suited for large-area applications, the results can clearly be taken as another confirmation that the ETA cell concept constitutes a feasible route towards efficient solar cells.

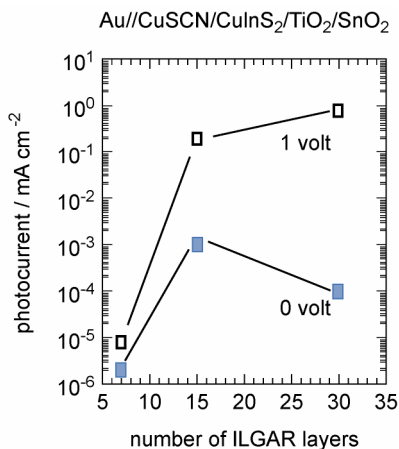


Figure 6.24 Photocurrents extracted from CuInS₂ absorber layers in nanoporous TiO₂ substrates for short-circuit (0 volt) and reverse-bias (1 volt) conditions.

6.5.2 CdTe-based solar cells

Electrodeposition of CdTe on nanoporous TiO₂ substrates predominantly produces coverage on top of the TiO₂ film, rather than a conformal or void-filling growth within the TiO₂ films. The morphology of the TiO₂ substrate was therefore altered and a spray pyrolysis process for the preparation of micro structured TiO₂ was developed. In this process a more open morphology was obtained with typical feature sizes in the nano- and micro-metre scale. The much coarser-grained surface allowed easier access for the dissolved precursors and fostered a higher degree of connectivity for the absorber material. These microporous TiO₂ films are shown in Fig. 6.4a.

Electrodeposition of CdTe, combined with a post-deposition annealing treatment, can lead to comparably efficient solar cells. Open-circuit voltages of 0.67 V and short-circuit currents of $\sim 9 \text{ mA cm}^{-2}$ have been observed (Ernst *et al.*, 2003). Typically these CdTe/TiO₂ cells have a total thickness of 2 μm and a local absorber thickness of 150 nm. The surface enlargement amounts to a factor $\sim 10\text{--}15$. The CdTe coverage is conformal, but some surface smoothing for layer thicknesses beyond 100 nm is usually observed. The crystallite size in the CdTe films scales with the thickness up to $\sim 100 \text{ nm}$ and remains at that level for thicker films. The crystallite size does not change appreciably in post-deposition anneal treatments, which typically comprise exposure to CdCl₂ vapour in air at 430 C. Electrical measurements indicate that after the annealing process the CdTe is lightly *p*-type. The minority-carrier

diffusion length was estimated to be 130–170 nm in these films. Attempts to add CuSCN to act as a *p*-type transport layer showed a strong tendency for Cu–Cd ion exchange, and usually resulted in devices that were electrically shorted.

However, with the particular surface morphology of these films shading effects are not very severe, as discussed in the context of Fig. 6.2. The void-filling transparent layer can therefore be replaced by a metallic back contact that is directly deposited on the CdTe absorber. The resulting glass/SnO₂/TiO₂/CdTe/Au structure corresponds to the scheme shown in Fig. 6.2d. Experimental results obtained for these devices are given in Fig. 6.25. The cross-sectional scanning electron micrograph shows the conformal nanocrystalline CdTe layer to be in very close physical contact to the TiO₂, as expected from electrodeposition growth.

A detailed optical study of this cell structure indicates that the optical path enhancement in this arrangement is only approximately fivefold. Thus this cell should be considered as a moderate version of an extremely thin absorber cell, in which the transport length has been reduced by a factor 10–15 and the optical path is enhanced by a factor of five.

A numerical simulation of this cell based on a one-dimensional model has been carried out by Ernst (2001), Grasso *et al.* (2002) and by Burgelman and Grasso (2004). In the work of Ernst and Grasso *et al.*, the spectral response data could be simulated with reasonable accuracy using only a few adjustable parameters. These simulations confirm the electron diffusion length in the *p*-type CdTe films to be approximately 150 nm. The recombination centre density was found to be 10¹⁹ cm⁻³. These data indicate that the nanocrystalline CdTe films are of inferior quality than the material used in the conventional, planar CdTe solar cells, where diffusion lengths of 2 μm and defect densities of 10¹⁶ cm⁻³ are typical.

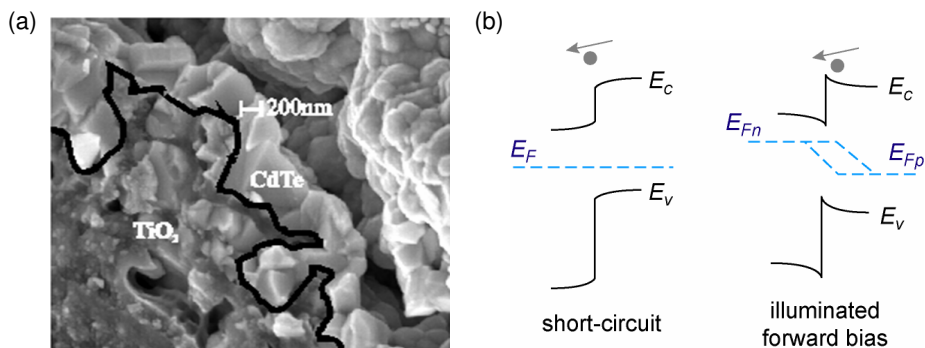


Figure 6.25 (a) TiO₂/CdTe interface in the CdTe ETA cell; (b) Band energy diagram under zero bias and forward bias, showing electron-transport barrier.

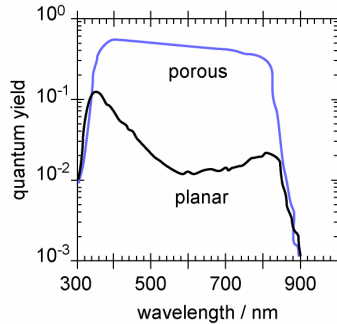


Figure 6.26 Spectral quantum efficiency spectra for CdTe/TiO₂ heterojunction cells on planar and microporous TiO₂ substrates at short-circuit conditions.

Figure 6.26 shows a comparison of the quantum efficiency between a planar and a structured cell morphology. The two cells in this comparison have been prepared in the same way, *i.e.* they have the same layer sequence and total absorber thickness, and are likely to have very similar material properties. The only difference between the two cells is the morphology of the TiO₂ substrate, which is planar in one case and microporous in the other. The comparison clearly demonstrates the advantages of the non-planar ETA cell arrangement, whose quantum efficiency in the visible region of the spectrum is more than a factor of 50 better than that of the planar sample. Based on these results we conclude that a non-planar cell arrangement may indeed be useful for incorporating medium and low-quality absorber materials in photovoltaic devices.

One of the remaining challenges for this first simple ETA cell is the large conduction-band offset between CdTe and TiO₂, which is approximately 0.6 eV. Numerical simulations, carried out by Grasso *et al.* (2002), indicate that, with this large offset, the cell develops a barrier-like potential spike under forward bias, as indicated in Fig. 6.25b. This spike becomes effective at a forward voltage of a few tenths of a volt, and leads to a marked reduction of the electron-transfer probability from the absorber to the TiO₂. As a consequence the photocurrent of the cell collapses around 0.2 V and the cell has a very low fill factor. Several attempts have been made to improve this situation, among them the insertion of an interface dipole layer to reduce the conduction band offset, the introduction of higher doping levels in the TiO₂, and doping the CdTe layer. A substantial improvement in the fill factor has, however, not been obtained with any of these changes.

These early experiments have recently been complemented by work of Belaidi *et al.*, (2003), who alloyed the CdTe absorber with Hg to decrease the band offset at the CdTe/TiO₂ interface. HgCdTe alloy films were prepared by adding small amounts of

HgO_2 to the $\text{CdSO}_4/\text{TeO}_2$ /ethanol solution used in the electrodeposition process (Neumann-Spallart, 1990). It is well established that, with increasing Hg content, a bandgap narrowing is induced, which is mostly due to a lowering of the conduction-band edge (Herman, 1985).

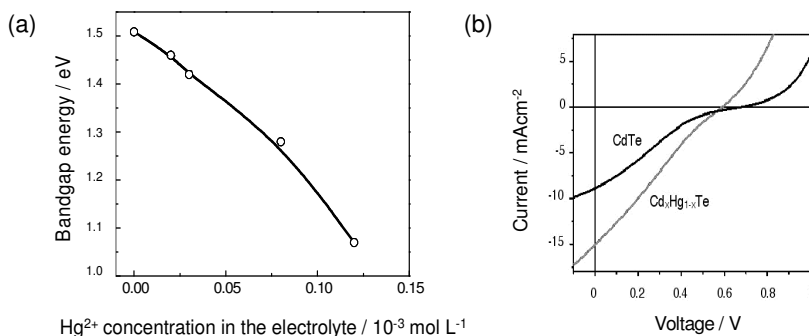


Figure 6.27 (a) Optical bandgap of $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ absorber layer estimated from absorption measurements as a function of Hg concentration in the electrolyte; (b) Comparison of the current–voltage characteristics for cells with CdTe and $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ absorber layers. AM1 simulated sunlight at 100 mW cm^{-2} was used.

Figure 6.27a shows the behaviour of the optical bandgap as the Hg concentration increases, as estimated from transmission measurements on $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ films on planar substrates. The spectral response of the $\text{TiO}_2/\text{Hg}_x\text{Cd}_{1-x}\text{Te}/\text{Au}$ cell is increased appreciably in the red part of the solar spectrum for absorber layers with bandgaps in the range $1.46 \text{ eV} > E_g > 1.28 \text{ eV}$. For smaller bandgaps, the spectral response decreases owing to a reduced electron transfer probability at the interface. This finding is in agreement with earlier findings (Hoyer and Könenkamp, 1995) which suggest that for band offsets larger than $\sim 0.25 \text{ eV}$, electron transfer into TiO_2 becomes inefficient. A comparison under simulated sunlight of the current–voltage characteristics for CdTe and $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ cells shows an improvement in short-circuit current by more than 50%, while the fill factor and open-circuit voltage remain largely unaffected (Fig. 6.27b).

6.5.3 Quantum dot-based ETA cells

Nanoporous substrates may also be considered as an ideal matrix material for quantum-dot absorbers. Due to their large internal surface a sufficiently high concentration of quantum dots can be placed in a TiO_2 layer of $\sim 5 \mu\text{m}$ thickness to

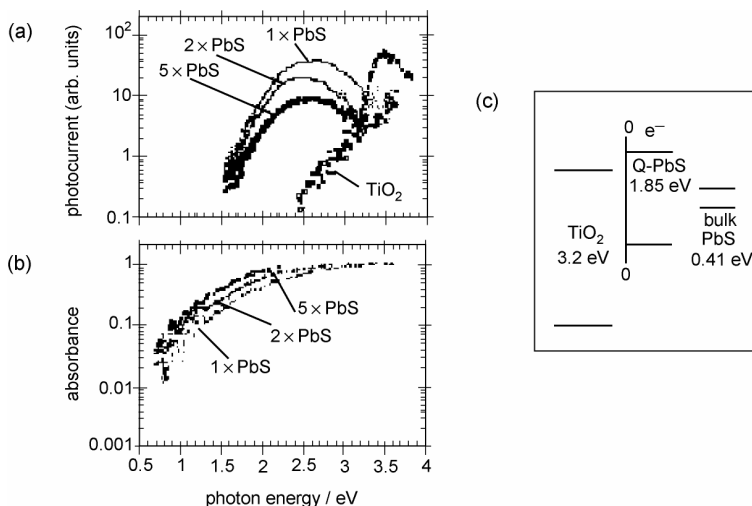


Figure 6.28 (a) Photocurrent spectra for a quantum dot in a PbS/TiO₂ heterojunction film, showing efficient sensitisation of the wide-gap TiO₂. When the number of PbS coatings is increased, the quantum dot size increases and electron transfer into the TiO₂ involves longer path lengths. Both effects reduce the transfer probability; (b) Absorbance spectra for the same films. The absorbance indicates that the dispersion of quantum dots also comprises a sizeable portion of quantum dots whose bandgap is too small to allow electron transfer into the TiO₂ conduction band; (c) Transfer scheme for electron transfer, showing the relevant electron energies for quantum dots and bulk PbS.

absorb a useful fraction of incident solar illumination. Figure 6.28 shows the absorbance and photoconductance spectra of a nanoporous TiO₂ film covered with PbS quantum dots with a density of $\sim 10^{16} \text{ cm}^{-3}$. It is seen that the absorbance approaches 100% for most of the visible solar spectrum. The PbS quantum dots can be deposited in an extremely simple process, which includes metal salt deposition from solutions followed by a chemical reaction with sulphur, also in the liquid phase. The same procedure allows the deposition of many other sulphides, as reported by Weller *et al.* (1994). The size distribution of these quantum dots is approximately Gaussian with a width corresponding to $\sim 20\%$ of the average size.

For PbS quantum dots, this size distribution gives a variation in bandgap between 0.8 eV and 2.3 eV. The transfer scheme for electron injection from the quantum dot into the TiO₂ matrix is indicated in Fig. 6.28c. Since only quantum dots with a bandgap $> 1.85 \text{ eV}$ can transfer electrons from the PbS conduction band into the TiO₂ conduction band, quantum dots of diameter $> 35 \text{ \AA}$ do not contribute to the photocurrent response but only to the absorbance. Accordingly, the absorbance and response spectra are expected to differ significantly for photon energies below

~ 1.85 eV, as borne out in Fig. 6.28b. Although some experimental effort has been invested in the fabrication of all-solid-state devices (Wienke *et al.*, 2003), conversion efficiencies have so far remained well below 4%. Better efficiencies have been obtained only with the use of a hole-collecting liquid electrolyte. So far no conclusions have been drawn from this finding, but it appears likely that the higher electrolyte conductivity may constitute a distinct advantage for extracting carriers from a structure of nanometre scale.

More recently inorganic quantum dots and nanowires have successfully been incorporated into organic and polymer solar cells by several groups (see for example Huynh *et al.*, 2002). However, the conversion efficiencies in these cells have so far been below 2%. It has been concluded that an intimate electrical contact with excellent charge transfer characteristics can be established at the inorganic/organic interface (Yin and Alivasatos, 2006; Robel *et al.*, 2007). The finding of these limited efficiencies may therefore again be due to the lower bulk conductivities in today's organic semiconductors as compared to the conductivities in liquid electrolytes.

6.6 Advanced photovoltaic concepts and new routes to other electronic devices

6.6.1 Novel photovoltaic concepts

The strong electron localisation in quantum dots is the basis of an interesting suggestion for the fabrication of solar cells exploiting a two-step excitation mechanism, as illustrated in Fig. 6.29. In principle, a two-step excitation mechanism allows the harvesting of photons with energy below the absorber bandgap. As shown by Luque and Marti (1997), energy conversion efficiencies as high as 56% can in

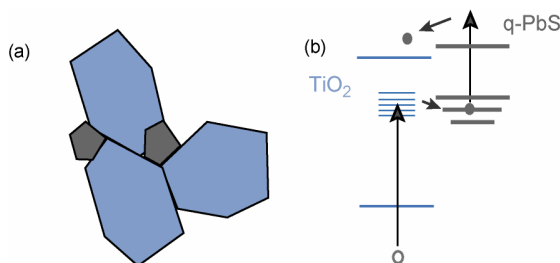


Figure 6.29 (a) Spatial arrangement for embedding quantum dots into the grain structure of nanoporous TiO_2 ; (b) Excitation scheme for two-step photon absorption in the PbS/TiO_2 heterostructure, involving excitation from the TiO_2 valence band to TiO_2 surface states, to PbS quantum-dot states, to PbS excited states and finally to TiO_2 conduction-band states.

principle be attained, which is similar to values obtainable in tandem cells. The two-photon excitation mechanism envisioned here involves real intermediate electron states with energy approximately halfway between the ground state and the final excited state. The intermediate states can arise from localised defect states, a defect band or a band of extended states as in a band structure with two bandgaps. A detailed theoretical study indicates that such a two-bandgap structure may indeed exist in a number of compound materials (Wahnon *et al.*, 2002).

As nanoporous materials are known to have a large density of surface states with energy in the bandgap, these materials may lend themselves to a two-photon excitation scheme of this kind. Figure 6.29 shows a scheme for nanoporous TiO_2 and a smaller-bandgap, localised absorber, such as quantum-size PbS. Here an electron is excited from the TiO_2 valence band to a localised surface or interface state and from there transferred to a state in an adsorbed quantum dot. The transfer involves a spatial charge separation, which is expected to substantially lower the probability of back recombination with the valence-band hole. From the quantum-dot state, the excited electron is excited in a second step to the conduction-band states of the quantum dot, and from there, in a second charge-transfer step, into the TiO_2 conduction band.

The process with the lowest excitation probability is the first excitation, from the TiO_2 valence band to its surface state. Using an intricate electrochemical method for a determination of the quantum efficiency, we were able to show that this excitation occurs at a probability of $\sim 10^{-4}$ (Bayon and Könenkamp, unpublished). While this efficiency is indeed quite low, it should be borne in mind that these were only first experiments. Considerably more work is needed to establish and understand the feasibility of this suggestion.

Concepts for tandem arrangements have been suggested for dye-sensitised solar cells using dye sensitisation at both electrodes and an electrolyte that provides the coupling between the two dyes (He *et al.*, 2000). A similar concept appears feasible also for solid-state devices, although it has not been explored yet in the context of ETA cells.

With sufficiently thin absorber layers, particularly with quantum-dot absorbers, it also appears possible to harvest hot carriers and reduce the thermalisation loss in solar cells. This idea was pursued at an early time by Cooper *et al.* (1983). Hot electron transfer has been demonstrated in an electrochemical arrangement, and the possibility of hot-carrier transfer across solid interfaces is starting to be realised. Furthermore, the associated phenomenon of multiple exciton generation from a single hot electron-hole pair created by a single photon within a semiconductor quantum dot has now been realised, as Art Nozik discusses in Chapter 3.

6.6.2 Transistors and LEDs

It is interesting to note that several non-photovoltaic devices have been explored using the processing and materials know-how discussed in this chapter. For example, using CuSCN nanowire columns in nanostructured polymer templates, a vertical nanowire field-effect transistor has been built. Potential applications of this embedded device may be as a pressure or contact sensor in ‘smart’ skins or in flexible displays (Chen and Könenkamp, 2003). Free-standing ZnO nanowires of the type shown in Fig. 6.3c and grown in electrodeposition on transparent SnO₂ substrates have been combined with organic insulators to produce broadband light-emitting diodes (Könenkamp *et al.*, 2004). While these new devices are presently still at proof-of-concept level, they appear to confirm the basic idea that, with a reduction in feature size, there will be a higher tolerance of defects, be they bulk or surface-related, since electronic transport paths are reduced and requirements on transport properties are less stringent. This may indicate that, as in the work in photovoltaics presented in this chapter, other research fields and applications may profit from new and possibly simpler processes, less expensive materials and new non-planar geometries.

6.7 Summary

Extremely thin absorber layers may open a new way to obtain inexpensive and, at the same time, efficient inorganic solar cells. This expectation is based on the realisation that short transport distances in the absorber and long optical paths can be obtained in heterostructures with extended junction areas. The anticipated effects contribute to better usage of material and permit less stringent quality requirements. The present state-of-the-art indicates that this expectation is well founded.

Using nanocrystalline CdTe as an absorber on microporous TiO₂ substrates, new types of solar cells with promising performance have been demonstrated in recent years. Several other design schemes, involving new materials, new geometries and new optical effects, are currently being explored. Solution growth techniques, particularly electrodeposition, are very versatile tools in the preparation of non-planar devices, since they allow the transport of precursor materials into very deep structures. When preferential surface attachment is exploited, continuous and extremely thin films can be deposited on nearly arbitrary substrates. Some of the more recently developed solution methods also allow the deposition of quantum-dot films. Gas-phase reactions can be integrated into the solution growth techniques.

While purity, crystallinity and defect densities are not always optimal in depositions laid down by inexpensive methods, non-planar devices with energy conversion efficiencies of up to 5% have now been demonstrated. This development confirms the initial expectation that new device geometries may indeed open a broader materials development. Moreover, recent developments in photovoltaics may spin-off into other electronic applications, such as transistor, sensor and LED development.

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ORGANIC DONOR–ACCEPTOR HETEROJUNCTION SOLAR CELLS

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The beginning is the most important part of the work.

Plato (427–347 BC), The Republic.

7.1 Introduction

7.1.1 *The case for plastic photovoltaic material*

Low-cost semiconductor materials and facile fabrication routes for photovoltaic (PV) junctions have been longstanding goals of photovoltaic materials research. The cost of photovoltaic electricity from conventional, silicon-based solar cells has decreased steadily over the past decade, but at a rate determined primarily by economies of scale (Anderson, 2001). Although market expansion driven by this reduction has been rapid, at an average of over 30% over the period 1996–2006 (IEA-PVPS, 2006), growth at this rate means that photovoltaic power is unlikely to provide a significant fraction of global electricity by 2040, and therefore may be unable to help meet national and international targets for low-carbon electricity generation. More rapid and widespread implementation of photovoltaic electricity generation requires other developments. In particular, technological innovations that reduce the cost of photovoltaic electricity substantially could drive a rapid expansion in implementation of photovoltaic technology.

Among the material systems currently of interest for this reason are the group of molecular-based materials combinations often referred to as ‘organic’ or ‘molecular’ photovoltaic materials. These refer to conjugated molecular species, such as polymers, molecules and dyes, which are capable of absorbing light and conducting charge and thereby acting as organic semiconductors. Their attraction lies primarily in the possibility of processing such materials directly from solution, and so fabricating

large-area thin semiconductor films using techniques similar to those used in the manufacture of plastic films. In the words of the most optimistic advocates of organic photovoltaics, the solar cells could be “painted on”. With bulk synthesis of the chemical materials and bulk solution processing of photovoltaic modules, the cost of the photoactive material could fall by an order of magnitude compared even with thin-film inorganic semiconductors. Additionally, the less exacting manufacturing environment, compared, for example, with crystalline silicon wafer production, promises to reduce the capital cost for production facilities and to make the technology more widely accessible, especially in developing countries. The low manufacturing and capital costs encourage dispersion of the technology (*i.e.* more local and smaller-scale photovoltaic generators) and make the technology highly compatible with decentralised power generation.

Apart from the promise of low cost, molecular photovoltaic materials offer the distinct advantages of compatibility with flexible substrates and, uniquely, the potential to vary the colour of photovoltaic modules by altering the chemical structure. Although compatibility with flexible substrates is possible with some thin-film inorganic photovoltaic materials, it is more easily and naturally achieved via solution deposition of extremely thin layers. Tuning of colour via molecular structure is a property unique to molecular semiconductors and is of particular value in building integration, where colour is of aesthetic importance, and in dual-function applications, such as photovoltaic windows, where a semi-transparent structure is required.

For the purposes of this chapter we will include conjugated polymers and ‘small’ conjugated molecules as organic photovoltaic materials. Solid-state dye-sensitised solar cells, which make use of an organic or metal-organic dye for light harvesting and an organic semiconductor as the hole transport layer, could equally well be classed as organic photovoltaic devices, but these are treated in Chapter 8 of this book and therefore are not discussed here.

7.1.2 *Properties of molecular semiconductors and comparisons with conventional semiconductors*

Molecular semiconductors include π -conjugated polymers and small molecular weight π -conjugated molecules based largely on carbon and hydrogen, with small amounts of oxygen, nitrogen and sulphur in some materials; Fig. 7.1 shows some typical structures. π -conjugation implies that the carbon atoms in the molecular backbone exist in the sp^2 rather than the fully saturated sp^3 hybridisation, such that three of the valence electrons per carbon atom are involved in tightly bound sp^2 orbitals and form

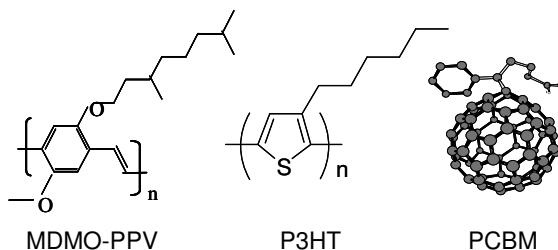


Figure 7.1 Chemical structures of some common organic photovoltaic materials: poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4 phenylenevinylene) (MDMO-PPV), poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM).

strong σ bonds with neighbouring atoms. The remaining electron occupies the more loosely-bound p_z orbital, and interacts with p_z orbitals on neighbouring carbon atoms to form weaker π bonds with those neighbours. The π orbitals are delocalised over several conjugated carbon atoms, typically over entire small molecules of molecular weight of 100–1000 and over a few (2–10) repeat units of a conjugated polymer. Conjugated segments tend to form planar structures and, in the solid phase, to interact with each other, leading to crystallisation in some cases, particularly in the case of flat or rigid conjugated segments. The π electrons can be excited from π -bonding to π^* -antibonding orbitals by photons with energies in the visible–UV part of the spectrum (2–4 eV). The resulting neutral excited state is called a singlet exciton and can be considered as the analogue of a bound electron–hole pair in a conventional semiconductor. Singlet exciton decay leads to visible light emission; the efficiency of this process led to the first applications of conjugated polymers to light emission (Burroughes *et al.*, 1990).

In the solid phase, molecules interact via weak van der Waals interactions with the result that excitons, and other excited states, are localised on the conjugated unit where they were created. The absence of strong intermolecular forces also tends to lead to disordered structures with large variations in molecular position, orientation and conformation. An isolated negative charge added to the π^* (antibonding) orbital interacts with the local molecular environment to form an electron polaron; this can move by a thermally activated, incoherent hopping process between molecules or conjugated segments. Similarly, an electron removed from the π (bonding) orbital leaves a hole polaron which is also mobile. As a result of the disorder in the molecular packing and the incoherent charge-hopping mechanism, charge mobilities in molecular semiconductors are very low, typically 10^{-7} – 10^{-1} cm² V⁻¹ s⁻¹. Molecular semiconductors can be doped to increase conductivity but doping can be detrimental to the optical properties and charge mobilities, and additionally, p - n junctions cannot be formed.

The following points of contrast between organic semiconductors and inorganic semiconductors, such as crystalline silicon, can be drawn:

- The organic semiconductor is sensitive to a smaller range of wavelengths in the solar spectrum;
- Excited states formed in organic semiconductors do not spontaneously dissociate into separate charges at room temperature;
- Electrostatic interactions are more important in organic semiconductors (partly because the relative dielectric permittivity is small, at typically 2–4);
- Charge mobilities in organic materials are much lower;
- Organic semiconductor layers are generally undoped, so the nature of electric contacts with the electrodes is strongly dependent on alignment of the intrinsic energy levels of the organic semiconductor with those of the contact metal.

As a result of these factors, the universal paradigm for inorganic solar cells, the p - n junction, cannot be adapted for organic semiconductors. The contrast with inorganic semiconductors is shown schematically in Fig. 7.2. The alternative of a metal–semiconductor–metal device structure, where photocurrent is directed by the difference in work function between the two metals, also cannot be used because the electric field created by available asymmetric contact materials is insufficient to separate the singlet exciton into electron and hole polarons. Therefore, alternative device architectures are needed.

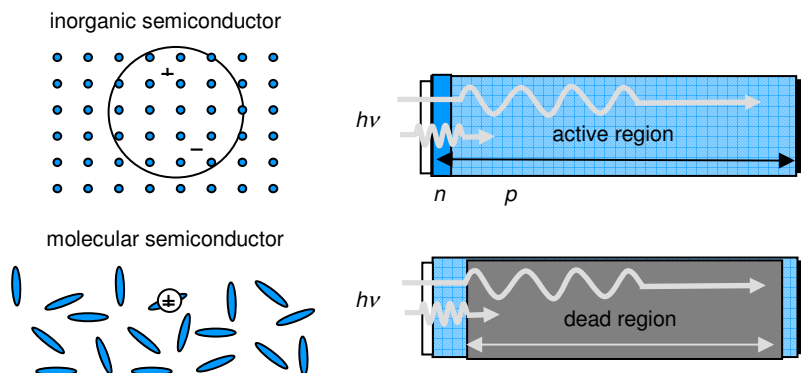


Figure 7.2 Upper panel: in a crystalline inorganic semiconductor, the photogenerated exciton is delocalised over many atoms and readily dissociates into electron–hole pairs, so a photon absorbed anywhere in an optically thick device generates separate charges. Lower panel: in an organic semiconductor, the photogenerated exciton is localised on a single molecule and dissociates into separate charges only when the exciton is created close to an interface. Therefore charge pairs are generated only in regions that lie within an exciton diffusion length of an interface.

In Section 7.2, the basic principles of photovoltaic energy conversion in organic semiconductors will be detailed. Next, in Sections 7.3 and 7.4, the main types of organic photovoltaic device will be outlined, along with recent developments and progress with each type of solar cell device. In Section 7.5, organic photovoltaics device physics will be discussed. In Section 7.6, current research efforts to address the challenges facing organic photovoltaic cells are summarised.

7.2 Basic principles of photovoltaic conversion in organic materials

7.2.1 Fundamental processes in organic semiconductors

The essential difference between organic and inorganic semiconductors is the degree of localisation of the excited states. This has the important consequences for photovoltaic conversion that, first, the excited state created by photon absorption does not spontaneously deliver an electron–hole pair at room temperature and, second, the charges, once separated, move relatively slowly through the material towards the electrodes. These features are critical in determining organic photovoltaic device design. The different device architectures used to achieve photoconversion in organic materials are reviewed in this section.

A central requirement of virtually all organic photovoltaic devices is an *interface* between two materials of different electronic properties, the purpose of which is to cause exciton dissociation. After photon absorption, the singlet exciton created in a molecular material can do several things. It can diffuse to other molecules or conjugated segments of the same material by a series of hops, it can decay radiatively by emission of a photon, it can decay into a more long-lived and lower energy *triplet* state, it can transfer on to a different type of molecule where the singlet exciton energy is lower (*energy transfer*) or it may *dissociate* via transfer of an electron or hole to another molecule or a metal electrode. Exciton dissociation can occur when the exciton reaches an interface with the other material and when it is most energetically favourable for the charges to separate, *i.e.* when the charge-separated state with electron and hole in different types of molecule has lower energy than the singlet exciton state in either material. This normally requires that the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels in one material are lower in energy than the respective LUMO and HOMO levels in the other, as shown in Fig. 7.3a. In addition, the offset in HOMO or LUMO energies between the two materials should be large enough to provide the energy, normally called the *exciton binding energy* E_B , needed to overcome the

coulombic attraction between the charges when localised on the same segment. We refer to the offset in HOMO (for hole transfer) or LUMO (for electron transfer) energies as the driving force, ΔE , for charge separation. Empirical and theoretical studies indicate that the minimum ΔE lies between 0.3 eV and 0.6 eV (Halls *et al.*, 1999; Bredas *et al.*, 2004), but this quantity is material-dependent and not well defined.

The materials which contain the electron and hole after charge separation are referred to as the electron *acceptor* and electron *donor*, respectively. Figure 7.3 illustrates the processes of exciton dissociation and energy transfer. Note that, although exciton dissociation can occur efficiently at the interface between an organic semiconductor and a metal electrode, the effective charge-separation efficiency at such an interface is limited because of the high likelihood of recombination of the separated charges at the metallic electrode.

Charge separation can thus be achieved by doping an organic semiconductor with molecules of a second material which acts as a donor or acceptor. To drive photocurrent, the separated charges should both be able to find pathways towards the electrodes, and therefore continuous phases of donor material between the charge-separation interface and hole-collecting electrode, and of acceptor material between the interface and electron-collecting electrode, are needed. The rate of charge transport from interface to electrode is controlled by the degree of order in the material, *i.e.* by the packing, density and orientation of molecular units.

A further consideration is the size of the domains of each material. For charge separation to occur, the exciton should reach the interface before it decays by another process. Radiative exciton decay typically occurs in hundreds of picoseconds. The distance that an exciton can diffuse in a molecular semiconductor on this timescale, called the *exciton diffusion length*, is typically a few nanometres. Therefore efficient light harvesting can occur only within approximately one exciton diffusion length (a few nanometres) of a donor–acceptor interface. Separated charges can also be lost via *recombination* at the interface. The more intimate the mixing, the higher the probability of opposite charges being found close to each other at the interface, and the higher the probability of recombination.

Sizing of the domains is therefore an optimisation problem: intimate mixing helps charge separation, but coarse mixing helps minimise recombination in favour of transport to the electrodes.

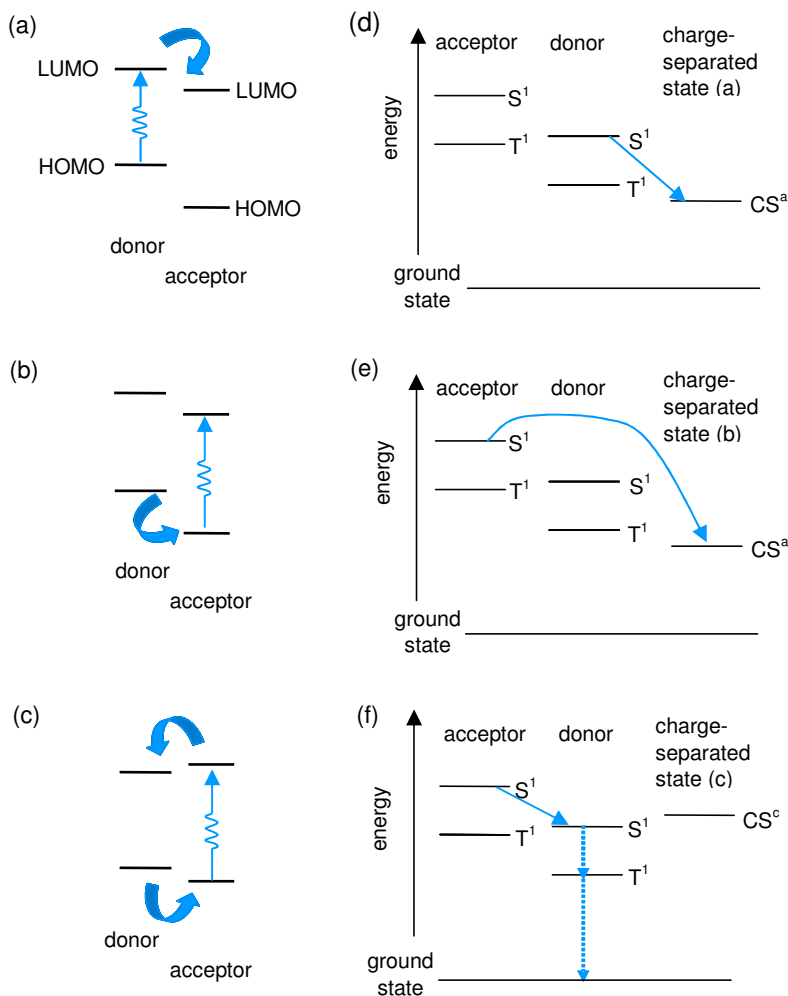


Figure 7.3 Energy-level diagrams of photoinduced (a) hole transfer (b) electron transfer and (c) energy transfer. Blue curled arrows show the direction of electron transfer in each case. In case (c), energy transfer occurs because the offset in HOMO levels is small and the energy of the charge-separated state is, as a result, larger than the exciton on the lower-gap molecule. (d), (e) Representation of the total energy of the species in cases (a) and (b), respectively. S^1 and T^1 represent the energies of the singlet and triplet excitons and CS represents the energy of the charge-separated state. In cases (a) and (b), the charge-separated state energy is lower than the triplet state of either donor or acceptor. (f) Representation of the total energy of the species in case (c). In (d), (e) and (f), blue arrows show the direction of energy transfer. The dotted arrow shows exciton decay to the ground state.

7.2.2 Molecular photovoltaic device types

All molecular photovoltaic device designs consist of a thin film incorporating continuous phases of donor and acceptor materials, sandwiched between two electrodes. Device types differ principally in the structure of the interface and the way the materials are put together. The simplest design consists of planar layers of donor and acceptor on top of each other, as shown in Fig. 7.4a. Excitons photogenerated in one or other material must diffuse to the central interface to dissociate. The separated charges are then driven to the opposite electrodes mainly by diffusion through the planar layer of the respective charge-transporting material. This bilayer structure has been developed in particular for vacuum-evaporated small-molecule devices (see Section 7.3). It has the advantage that the separated charges have a high collection probability, and photovoltaic action is not strongly sensitive to the nature of the two electrode materials. However, the thickness (and therefore the optical depth) is limited to the sum of the exciton diffusion lengths of the two materials, with the consequence that devices must be optically very thin, or that material quality must be very high (to extend the exciton diffusion length), in order to achieve a high incident-photon-collected charge efficiency.

A quite different design, which was responsible for widespread interest in the utilisation of conjugated polymers in molecular photovoltaic devices, is the dispersed or 'bulk' heterojunction (BHJ) device. In these devices, the donor and acceptor phases are mixed together to yield a blend film containing domains of each material. Various types of BHJ are available, differing mainly in the type of material and the way that they are deposited. The most widely studied variety consists of a blend of a soluble conjugated polymer with either a second polymer, a soluble small molecule or inorganic nanoparticles which are co-deposited from solution (Figs. 7.4b and c). For photocurrent generation from these devices, it is critical that the electronic properties of the two electrodes be sufficiently different. An alternative approach to co-deposition of a random blend is to prepare a rigid nanostructure of one component and apply the second component from solution so that it penetrates into the structure; this is used in organic-inorganic hybrid structures. The ideal structure for a BHJ is one containing columnar domains containing directed vertical transport paths, with spacing similar to the exciton diffusion length (Fig. 7.4d). These can be achieved using vertically oriented inorganic crystalline nanostructures or by exploiting self-organisation of molecular materials, such as discotic liquid crystals, which produce columnar phases. In the following we will refer to the material that absorbs light, potentially leading to charge separation, as the *active layer*, to distinguish it from other layers, such as electrodes and substrate.

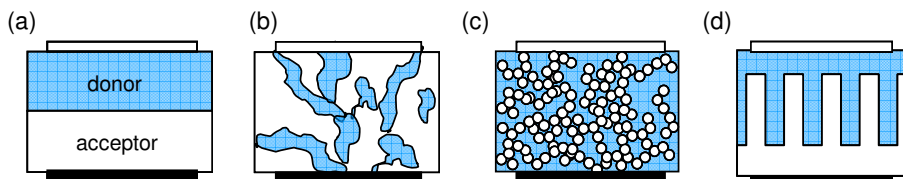


Figure 7.4 (a) A donor–acceptor bilayer heterojunction. Donor regions are shaded blue and acceptor regions are white. (b) A randomly organised donor–acceptor dispersed heterojunction. (c) A donor–acceptor junction based on acceptor nanoparticles dispersed in a donor matrix. (d) An ‘ideal’ donor–acceptor junction containing vertically aligned domains. In cases (a) and (d), charges separated at the interface are driven to the opposite electrodes by diffusion while in (b) and (c), charges separated at the interface rely on differences in the work function of the electrodes for direction of the photocurrent.

In addition to the requirements on the energy levels of donor and acceptor for interfacial charge separation, it is necessary that the work function of the electron-collecting electrode should be well matched to the LUMO of the acceptor material, and that of the hole-collecting material be well matched to the HOMO of the donor. In bulk heterojunctions, photovoltaic action can only be achieved if electronic contact is made to the photoactive material using suitable asymmetric electrodes. For high efficiency the electrodes should also be conductive and well matched in energy to the electron or hole transport levels. The constraints on electrode materials will be treated in more detail in Sections 7.5 and 7.6.5. The development and optimisation of bilayer and BHJ device types are reviewed in Sections 7.3 and 7.4 respectively.

7.3 Donor–acceptor bilayer devices

The first efficient bilayer solar cell, using vacuum-deposited layers of copper phthalocyanine (CuPc) as the donor and a perylene tetracarboxylic derivative as the acceptor, was reported by Tang and co-workers in 1986 (Tang, 1986). The bilayer design produced an order of magnitude increase in power conversion efficiency when compared with a single organic layer with the same device architecture. Since then buckminsterfullerene (C_{60}) has replaced perylene derivatives as the electron acceptor of choice in organic bilayer devices. Figure 7.5 is a schematic representation of a CuPc: C_{60} bilayer device. The reported HOMO energies of CuPc and C_{60} are 5.2 eV and 6.2 eV below vacuum level, respectively, and their LUMO energies are 3.5 eV and 4.5 eV below vacuum level (Peumans and Forrest, 2001). Thus the driving force both for hole transfer from CuPc to C_{60} and for electron transfer from C_{60} to CuPc is ~ 1 eV, large enough to drive exciton separation at the interface of the two materials.

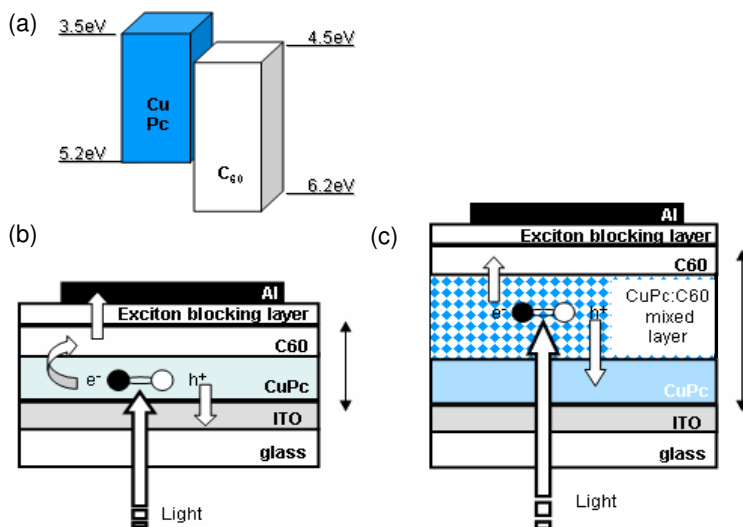


Figure 7.5 (a) Schematic showing HOMO and LUMO energy levels of CuPc and C₆₀. Energy levels are measured down from the vacuum level. (b) Device structure of CuPc:C₆₀ bilayer device. Exciton dissociation is facilitated at the planar donor-acceptor interface. (c) Device structure of a CuPc:mixed layer:C₆₀ device. Exciton dissociation can occur within the mixed layer, increasing the effective thickness for light harvesting (denoted by double-headed arrow).

Organic bilayer solar cells have improved steadily since the report by Tang in 1986. Developments have been assisted by detailed modelling and advances in the understanding of molecular materials, as well as by innovations in device design and fabrication techniques.

The highest efficiencies for bilayer heterojunction structures have been achieved using CuPc and C₆₀, with a maximum reported efficiency of 4.2% (Xue *et al.*, 2004a). Alternative donor materials that have been studied include zinc phthalocyanine (Drechsel *et al.*, 2005), tin(II) phthalocyanine, pentacene and novel low-optical-gap compounds. Rand *et al.* (2005) fabricated molecular-layer solar cells with 1% power conversion efficiency using a tin (II) phthalocyanine which extended the absorption of the device to beyond 900 nm. In another attempt to increase the light absorption throughout the visible and infrared portions of the solar spectrum, Yoo *et al.* (2004) produced solar cells from pentacene:C₆₀ bilayers with a power conversion efficiency of 1.5% and external quantum efficiencies of at least 40% in wavelength ranges from 400 nm to 700 nm. Several attempts have been made to improve the device performance of the original Tang structure using perylene as an electron acceptor, but the

efficiencies have still been low compared with fullerene-based devices (Hu and Matsumura, 2004). In a different approach, a low-optical-gap perylene dye can be introduced as a third component with the aim of extending absorption in a manner similar to that in a dye-sensitised solar cell (Gebeyehu *et al.*, 2004). A recent study by Pfeiffer and co-workers, focussed on increasing open-circuit voltage by optimising the interfacial energy steps, led to a power conversion efficiency of 3.4% using a novel oligothiophene donor of low optical gap and high ionisation potential (Schulze *et al.*, 2006).

Despite attempts to increase efficiency using lower optical gap materials, the highest power conversion efficiencies are still achieved using CuPc as the donor material and C₆₀ as acceptor. The most important improvements have come about through improved device design. Key developments include the following:

- Use of wide-gap transport layers to carry charges to the electrodes from the lower-gap active layers without risk of exciton quenching at the electrodes (Peumans *et al.*, 2000; Drechsel *et al.*, 2005).
- Use of optical design to optimise the position of the active layers within the multilayer structure (Peumans *et al.*, 2000).
- Doping of the transport layers to minimise series resistance, improve electronic matching with interfaces and increase robustness of the device with respect to variations in material or interface quality.
- Introduction of a mixed donor–acceptor layer in between the pure donor and acceptor layers, to increase the interfacial area for charge separation and thereby enable an increase in the optical depth without losses in light harvesting (Heutz *et al.*, 2004; Xue *et al.*, 2005).
- Annealing of the mixed layer to achieve optimum segregation of the phases in the mixed layer (Peumans *et al.*, 2003a).
- Use of tandem structures to enhance open-circuit voltage (Yakimov and Forrest, 2002). This is discussed in Section 7.6.1.

The highest efficiencies to date for single-junction bilayers have been obtained for multilayer structures containing a *p*-doped CuPc layer, an undoped mixed CuPc : C₆₀ layer, and an *n*-doped C₆₀ layer (Fig. 7.5c), taking advantage of the most important design features listed above. A serious limitation of perfectly planar bilayer structures is the relatively small volume of material in which efficient light harvesting occurs (the effective volume is $2AL_{\text{ex}}$ where A is the device area and L_{ex} the exciton diffusion length). Studies have established that charge separation is improved at interfaces with some degree of intermixing of the donor and acceptor materials. The increased interfacial area arising from this interdigitation of components increases the volume

available for interfacial charge separation. This increased interfacial area is achieved for molecular-layer films fabricated using vacuum evaporation by co-deposition of the donor and acceptor material, in some ratio, between the pure donor and acceptor layers (Drechsel *et al.*, 2004; Heutz *et al.*, 2004; Sullivan *et al.*, 2004; Schultes *et al.*, 2005; Xue *et al.*, 2005). If the donor and acceptor components each form connected phases within the mixed layer (whose morphology can be improved by thermal annealing (Peumans *et al.*, 2003a)), then the charge carriers can easily travel from the interface to their respective electrodes, and the effective volume for charge separation is increased by the entire volume of the mixed layer.

In addition to vacuum-deposited small-molecule structures, bilayer devices have been fabricated from conjugated polymers and other solution-processible materials. One study reports a 1.9% efficient device fabricated by lamination of two spin-coated polymer layers (Granstrom *et al.*, 1998). In principle, polymer bilayers can also be fabricated by spin-coating of successive layers using incompatible solvents. A more practical route to planar bilayers is the deposition of successive layers that have previously been spin-coated and removed from the substrate by a float-off technique (Ramsdale *et al.*, 2002).

Bilayer structures with roughened interfaces can be fabricated using conjugated polymer:small molecule combinations. In one approach, a polymer layer is spin-cast onto a small molecule (*e.g.* perylene) covered ITO surface in a solvent-saturated environment. The slow drying encouraged by the solvent atmosphere allows the polymer layer to penetrate into the rougher perylene matrix, resulting in an enhanced interfacial area for charge separation. Such devices had 1.9% efficiencies, which is a promising result for the materials used (Nakamura *et al.*, 2004).

Planar polymer bilayers do not lead to such high quantum efficiencies as polymer-based BHJ devices, but they provide an excellent arena for the development and testing of models of organic photovoltaic device behaviour. Studies of polymer bilayers have clearly demonstrated that the charge-separation process in these planar structures is driven by diffusion of separated charges away from the interface, and not by a potential difference between the electrodes. This marks a profound difference in the function of bilayer and BHJ solar cells, which will be discussed below, and also marks an important point of contrast with inorganic solar cells. Through modelling of bilayer systems, the dominant factors controlling the efficiency of organic bilayer devices have been identified as the interfacial energy-level alignment and the incident-photon-to-charge separation efficiency, which is controlled by both the effective optical depth and the interfacial exciton dissociation yield (Gregg and Hanna, 2003; Nelson *et al.*, 2004). Approaches to all of these factors are discussed in Section 7.6.

7.4 Donor–acceptor bulk heterojunction devices

7.4.1 Principles of bulk heterojunction devices

The term bulk heterojunction, introduced in Section 7.2 above, refers to a thin film containing phases of donor and acceptor materials with a large-area interface between them for charge separation. The concept was introduced in the mid-1990s through contemporary studies in Cambridge, Santa Barbara and Osaka (Halls *et al.*, 1995; Yu *et al.*, 1995; Yoshino *et al.*, 1997). The BHJ is particularly appealing because such structures can be formed naturally by casting solutions containing two components, usually a soluble conjugated polymer and another soluble conjugated molecule, thereby offering a facile fabrication route to a workable device architecture. Conjugated polymer-based BHJ structures are the most widely studied technology in organic photovoltaics. In this section we outline some basic considerations for BHJ devices and then review developments in BHJ device design and performance.

As outlined in Section 7.2 above, the BHJ increases the volume in which photo-generated charge separation, and therefore photocurrent generation, can occur relative to bilayer structures. This allows for more efficient light harvesting using optically-thick active layers. Figure 7.6 shows a cross section of a BHJ device.

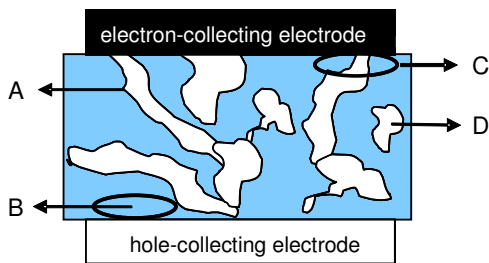


Figure 7.6 Schematic of bulk heterojunction (BHJ) film sandwiched between electron- and hole-collecting electrodes. The white region denotes the acceptor material, usually a fullerene derivative, and the blue region denotes the donor material, usually a conjugated polymer. Regions marked A and B assist charge collection, while regions C and D hinder performance. For directed photocurrent generation, the electrodes should collect only one type of charge carrier, and be blocking for the opposite charge carrier.

In Fig. 7.6, charge separation occurs when an exciton generated in either component of the active layer travels to a donor–acceptor interface where the local driving force between the materials provides the energy to dissociate the exciton into free charges. From this interface, the hole travels via a hopping mechanism through the donor material to the photocathode, or hole-collecting electrode and the electron

travels to the photoanode, or electron-collecting electrode. In order to produce a directed photocurrent, the electrodes should be selective. In the ideal case, the electron-collecting electrode should block holes, and the hole-collecting electrode should block electrons. Interconnected networks of the electron-transporting and hole-transporting materials, such as the region marked A in Fig. 7.6, are required to provide clear pathways for the charge carriers to reach their respective electrodes.

The active layers of BHJ devices are typically fabricated from organic solutions using spin-coating, drop casting, doctor blading¹ or dip-coating methods. In general, these processes offer little control over the size, shape and distribution of donor and acceptor domains in the active layer. The same casting process that leads to spontaneous large-area interface formation can also result in undesirable features. These include: (i) contact of one or both materials with both electrodes: if both materials are in contact with an electrode, as at region C in Fig. 7.6, back electron transfer can occur, acting as a shunt pathway; (ii) phase segregation into domains that are too large for efficient exciton dissociation; (iii) formation of isolated domains where separated charges become trapped, as illustrated by region D in Fig. 7.6; and (iv) unevenness in the film thickness (due to differing material properties), which can lead to charge leakage through the thinnest points. Most research on BHJ devices is focused on avoiding such unfavourable film properties through the control of the morphology and material properties of the active layer.

BHJ devices differ from bilayers primarily in the effect of the larger area interface, which enhances charge recombination as well as separation, and in the role of the electrodes. As detailed above, no work function difference between the electrodes in a bilayer device is necessary for photocurrent generation, because the asymmetry in the vertical structure *provides* a driving force for directed photocurrent. The concept is explained in detail in several reports (Ramsdale *et al.*, 2002; Gregg and Hanna, 2003; Nelson *et al.*, 2004). Electrode asymmetry can enhance the photovoltage, but is not necessary in order to produce one (Ramsdale *et al.*, 2002). In a randomly organised BHJ structure with no vertical compositional gradient, no preferred direction exists for charge transport apart from that which is due to the difference in electrode work functions. Therefore, the electrode asymmetry is essential for device function.

The open-circuit voltage of BHJ devices has been found to be correlated to the energy difference between the LUMO energy of the electron acceptor, $E_{\text{LUMO,A}}$ and the HOMO of the electron donor, $E_{\text{HOMO,D}}$ (Brabec *et al.*, 2001; Mihailetschi *et al.*,

¹ Doctor blading, also known as tape casting or knife coating, uses a scraping blade, known as the 'doctor' for the removal of excess substances from a moving surface being coated.

2003; Mihailetchi *et al.*, 2004), when the electrodes of the device make ohmic contacts with the acceptor and donor materials. Progress in understanding the origin of the open-circuit voltage of organic solar cells and its dependence on device parameters will be discussed in Section 7.6.2 below.

To achieve high efficiency in organic bulk heterojunction devices, electrodes should be asymmetric, conductive and well matched in energy to the electron and hole transport levels of the active layer. These conditions are hard to meet because, first, both the electron-transporting and hole-transporting phases are generally in contact with both electrodes. If the electrodes are not perfectly selective, then charge leakage can occur, reducing the open-circuit voltage and fill factor. Second, the active layer is normally undoped so that low-resistance contacts with metals are hard to achieve, and the quasi-Fermi levels within the active layer are highly sensitive to variations in charge density and defects. Third, a limited range of electrode work functions is available, which do not match well with HOMO or LUMO levels of available donor and acceptor materials. The most commonly used electrodes are indium tin oxide (ITO) coated with poly(3, 4-ethylenedioxythiophene):poly(4-styrene sulphonate) (PEDOT:PSS) as photocathode, and aluminium with another low work function metal, such as calcium, as photoanode. These materials have the specific problems that ITO is costly, unstable under prolonged operation, and not sufficiently selective; water-based PEDOT:PSS is prone to absorb water, thereby losing conductivity and reducing the lifetime of the active materials; low-work-function metals tend to oxidise and lose conductivity. These features lead to the twin pitfalls observed in organic bulk heterojunction devices: either poor electrode *selectivity* leads to shunt losses, with a reduction in fill factor and a reduction in photovoltage below the value expected from the electron- and hole-transport levels, or slow *charge transfer* to the electrode, due either to poor conductivity or poor electronic matching, leads to a resistive loss in fill factor and loss in photocurrent. Optimisation of electrode properties is required even for the best materials used to date, and the problem of electrodes promises to be even more important for as-yet untried materials, especially those of very different electronic properties.

7.4.2 Progress with polymer:fullerene bulk heterojunction devices

Bulk heterojunction device performance has improved by strides since the first reports of charge separation in bulk heterojunctions, with power conversion efficiencies that now approach 5% (Li *et al.*, 2005; Reyes-Reyes *et al.*, 2005; Kim *et al.*, 2006a). Studies have focused on varying the donor and acceptor materials, optimising the

donor : acceptor ratio in the active layer, varying fabrication methods and introducing techniques to control phase morphology within the active layers. Several groups of conjugated polymers, including poly(*para*-phenylenevinylene)s (PPVs), polyfluorenes and polythiophenes, have shown promise as the donor component. While several alternative materials, including electron-transporting polymers, and small molecules such as perylene and silole derivatives, have been evaluated as the electron acceptor, the highest solar cell device performances have consistently been achieved using fullerene derivatives. The reasons for the superior performance of fullerenes are not well understood, but may include the high electron mobility and high electron affinity of C₆₀. Additional factors influencing fullerene performance in organic solar cells are the nature of the interactions formed between donors and fullerenes, and the electronic structure of fullerene itself: C₆₀ fullerenes possess a small singlet–triplet energy splitting, which means that triplet formation is efficient and triplet states may contribute to energy transport. The majority of research in the field of organic photovoltaics to date has focused on the fullerene [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM), blended with PPV or polythiophene derivatives.

The first material system to be studied extensively was the blend of poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4 phenylenevinylene) (MDMO-PPV) with PCBM, and these studies have provided a large experience base to guide optimisation of other material systems for the future. Here we mention some key findings. First, it was established that the choice of solvent for spin-coated films has a striking effect on the performance of MDMO-PPV : PCBM solar cells (Shaheen *et al.*, 2001). Chlorobenzene-processed devices yielded power conversion efficiencies of 2.5% compared with 1% for devices processed from toluene. Microscopic studies (Martens *et al.*, 2003; van Duren *et al.*, 2004) revealed that toluene allowed large domains of crystalline PCBM to form in the film, reducing the area available for charge separation, while the more polar chlorobenzene leads to more intimate mixing of material components and therefore to a larger interface for charge separation (Fig. 7.7). This observation led to a simple lesson: the morphology of bulk heterojunction structures matters, and it can be controlled via material processing.

Optimisation of the MDMO-PPV : PCBM blend film composition showed that the highest currents and power conversion efficiencies are achieved when the ratio of MDMO-PPV to PCBM is 1:4 by weight (Scharber *et al.*, 2003; van Duren *et al.*, 2004; Mihailetschi *et al.*, 2005). This is initially surprising because one might expect that, in order to maximise the photocurrent, one would need more of the component that absorbs light more efficiently (the MDMO-PPV polymer), and, in order to balance electron and hole drift currents, more of the component with the lower charge mobility (again, the polymer). Yet the winning composition contains a large excess of

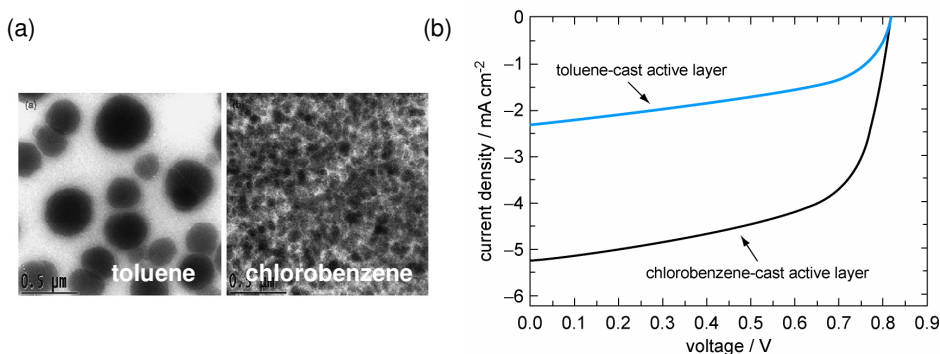


Figure 7.7 (a) Transmission electron microscope images of 1:4 MDMO-PPV:PCBM films cast from toluene (left) and chlorobenzene (right) solutions (Martens *et al.*, 2003). (b) Current voltage characteristics of devices made from the two types of film. The chlorobenzene-produced device produces more than twice the short-circuit current of the toluene-produced device (Shaheen *et al.*, 2001).

PCBM. The contradiction has been explained by the observation that the hole mobility in the blend is higher than in the pristine MDMO-PPV polymer, increasing dramatically with PCBM content (Mihailetchi *et al.*, 2005; Tuladhar *et al.*, 2005), and additionally by the argument that the higher dielectric permittivity of PCBM will encourage charge separation in a PCBM-rich film. Differences in the type of morphology achieved with PCBM content is also a contributing factor (van Duren *et al.*, 2004). These studies provide a second important lesson: the properties of the blend film are not the same as the sum of the properties of the parts.

Following on from studies of MDMO-PPV:PCBM, the blend system consisting of regioregular poly(3-hexylthiophene) (P3HT) with PCBM emerged as the foremost material combination for BHJ devices, with power conversion efficiencies in the range of 4–5% (Li *et al.*, 2005; Reyes-Reyes *et al.*, 2005). P3HT was originally chosen as an alternative to MDMO-PPV because it absorbs light at longer wavelengths (optical gap of ~ 1.9 eV compared with 2.1 eV for MDMO-PPV) and shows higher hole mobility. These combined factors lead to a potential doubling of the photocurrent produced in a P3HT:PCBM compared with an MDMO-PPV:PCBM device. However, P3HT has proved extremely promising for another reason: the nanoscale morphology of the P3HT:PCBM blend film is sensitive to solvent and processing, and can also be manipulated through post-processing methods such as thermal annealing. Annealing of P3HT:PCBM solar cells above the glass transition temperature of the polymer improves the efficiency of the device by a factor of almost two owing to the crystallisation of P3HT domains in the active layer of the solar cell (Chirvase *et al.*, 2004; Yang *et al.*, 2005). Detailed studies of the morphology formed

show that crystallisation of both components occurs, resulting in a morphology with a finite degree of phases segregation, and where the crystalline polymer domains help to restrict the growth of the PCBM domains. Studies have shown that the phase-segregated domain structure can be achieved by a range of processing techniques, including control of the solvent and the atmosphere as well as thermal annealing, and that the higher the degree of crystallinity of the polymer, the higher the device performance. These morphology studies lead to the conclusion that a certain degree of phase segregation is necessary for optimum performance. Additionally, the high charge mobilities in P3HT mean that relatively thick films of P3HT:PCBM can be used in devices, leading to more efficient light harvesting.

7.4.3 Progress with polymer:polymer bulk heterojunction devices

Polymer–polymer photovoltaic devices have continued to attract interest since the first bulk heterojunction devices were made in the mid-1990s (Halls *et al.*, 1995), driven by the ease of processibility of conjugated polymers and the developing applications of polymer-blend films in light emission. However, progress in device performance has been slower than with polymer:fullerene bulk heterojunctions. A key issue is the length scale of phase separation of donor and acceptor components that can be achieved by solution casting of the polymer blend. Detailed studies have demonstrated that polymer:polymer blend films show large-scale phase separation in their surface morphology which is very much dependent on the solvent used for film preparation, film-casting methods and post-processing conditions (Halls *et al.*, 2000). However, the degree of mixing achieved appears to be coarser than for polymer:fullerene blends, and the photon-to-current quantum efficiencies are correspondingly lower. In one study of a ternary donor:polymer acceptor:polymer fullerene system, photocurrent increased steadily with the ratio of PCBM to electron-accepting polymer, with corresponding improvements in the morphology as measured from the packing of the donor component (Kim *et al.*, 2007). The lower electron mobility of electron-accepting polymers compared with fullerenes may also contribute to the poorer performance of polymer:polymer blend devices.

A second important factor in polymer:polymer blend device design is the degree of vertical segregation of donor and acceptor polymers. This can be controlled by choice of solvent and processing (Arias *et al.*, 2002), by thermal post-treatments (Veenstra *et al.*, 2004) or by solution casting of consecutive layers. Vertical segregation can greatly improve the device shunt resistance. Currently, the best efficiencies for polymer–polymer solar cells is 1.5% for a blend of a PPV polymer with a red

polyfluorene (Koetse *et al.*, 2006). This performance is a major improvement on previous results, and benefits from dedicated synthesis of new electron-accepting polymers and from processing techniques that optimise morphology.

Despite the relatively low power-conversion efficiencies of polymer:polymer blend devices, they have proved to be useful architectures for study of the mechanisms of photoinduced charge separation and charge recombination. Morteani and co-workers observed that an intermediate excited state, called an *exciplex*, of character intermediate between an exciton and an electron–hole polaron pair, is formed in blends of two polyfluorene polymers (Morteani *et al.*, 2003; Morteani *et al.*, 2004). The exciplex alters the energetic barriers for interfacial charged transfer and may be centrally involved in mediating charge separation and recombination at organic heterojunctions. Intermediate excited states have also been observed in other types of bulk heterojunction films, specifically polymer:fullerene blend films (Benson-Smith *et al.*, 2007). A clearer picture of charge separation events is crucial for the development of plastic solar cells and further study of exciplex states may point the way for progress. Polymer:polymer blends are ideal model systems for the study of these emissive intermediate states, so the study of such blend films is central to the search for a clear physical model of charge separation in bulk heterojunction devices.

7.4.4 Hybrid polymer: inorganic nanostructure bulk heterojunction devices

An alternative type of donor:acceptor heterojunction device consists of an organic semiconductor as donor and an inorganic semiconductor component, such as a II–VI compound semiconductor or a metal oxide, as the electron acceptor. Such structures are often referred to as ‘hybrid’ devices; they have recently been reviewed by Bouclé *et al.* (2007). Crystalline and nanocrystalline inorganic semiconductors have several attributes as electron acceptors, including relatively high electron mobility, high electron affinities, and good physical and chemical stability. Solution-processible semiconductors that can be prepared in different nanocrystalline morphologies offer the potential for a large area interface when combined with a solution-processed organic component. II–VI and I–III–VI compound semiconductors also offer optical absorption in the red part of the spectrum, and can therefore be used to enhance light harvesting. This aspect is discussed in greater detail in Section 7.6.1. Titanium dioxide (TiO₂) has been used in several approaches for hybrid organic–inorganic solar cells, following the observation of efficient photoinduced electron transfer to TiO₂ from various polymers (Savenije *et al.*, 1998; Salafsky, 1999; Arango *et al.*, 2000). TiO₂ is interesting as a cheap and non-toxic material which can be prepared in a wide

range of nanostructured forms by solution chemical methods, can be used in light-trapping structures (on account of its high dielectric permittivity), and benefits from a wide experience base from dye-sensitised solar cell research. Zinc oxide (ZnO) is an alternative that offers a very high electron mobility and high electron affinity.

Two approaches to the bulk heterojunction hybrid organic–inorganic solar cell have been pursued: (1) nanostructured, layered devices, where polymer is inserted into the pores of a nanostructured electrode consisting of sintered nanoparticles (Ravirajan *et al.*, 2004; Ravirajan *et al.*, 2005a), aligned nanorods (Olson *et al.*, 2006; Ravirajan *et al.*, 2006) or a templated porous film (Coakley and McGehee, 2003); and (2) polymer:nanoparticle blend devices where semiconductor nanoparticles and polymer are deposited from the same solution. The conjugated polymer:porous TiO₂ layered structures have led to power conversion efficiencies of 0.58% (Ravirajan *et al.*, 2005b) and a clear demonstration of the increase in photocurrent available by nanostructuring the electrode relative to a polymer:TiO₂ bilayer structure (Ravirajan *et al.*, 2004). While they offer good electrode selectivity, the layered structures are limited by imperfect infiltration of polymer into the pores of the nanostructure, which limits the device thickness and the photocurrent.

The best performances for the hybrid blend approach have been reported for blends of conjugated polymers with visible-light-absorbing inorganic nanocrystals such as cadmium selenide (CdSe) (Huynh *et al.*, 2002; Sun *et al.*, 2005). Polymer:lead sulphide (PbS) blends also offer very promising photocurrent densities on account of the low optical gap of PbS (Watt *et al.*, 2005). For blends of polymers with non-absorbing nanoparticles, an MDMO-PPV:ZnO nanoparticle blend device showed a projected efficiency of 1.5% and high external quantum efficiency of 40%, indicating very efficient charge separation (Beek *et al.*, 2004). Blend devices of TiO₂ with conjugated polymers have not yet performed well, partly because of difficulties in optimising the blend film morphology and charge trapping within the TiO₂; the highest reported efficiency is 0.49% (Zeng *et al.*, 2006). The main challenge for polymer:nanoparticle blend devices is achieving effective conductive paths between the nanoparticles for electron collection. This has been tackled by using elongated nanoparticles randomly dispersed in a polymer (Huynh *et al.*, 2003) or vertically grown on a substrate (Olson *et al.*, 2006; Ravirajan *et al.*, 2006), which improves electron transport in the blend by reducing the number of inter-particle hopping events (Fig. 7.8). CdSe tetrapods have been successfully incorporated into cells with a poly-(phenylenevinylene) derivative, leading to efficiencies up to 2.8% as a result of the partial vertical alignment of the nanocrystals (Sun *et al.*, 2005; Sun and Greenham, 2006). Promising as the polymer-nanocrystal systems appear, the use of toxic precursors (Cd, Pb, *etc.*) remains an inhibitor to their large-scale development.

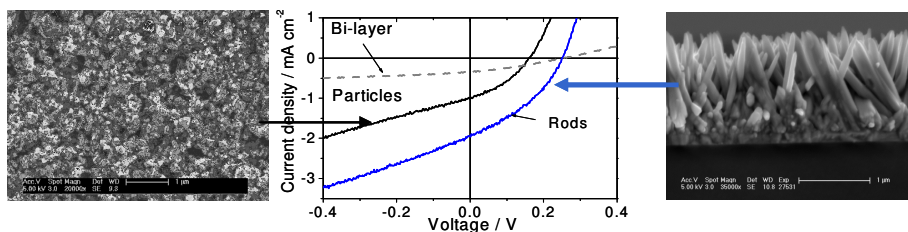


Figure 7.8 Centre: Current density–voltage characteristics of hybrid poly-3-hexylthiophene:ZnO devices with different morphology. The device based on a layer of vertically oriented ZnO nanorods outperforms the device based on ZnO nanoparticles of similar diameter, while both nanostructured films outperform the bilayer. Left: Scanning electron microscope image of ZnO nanoparticle film. Right: SEM image (side view) of ZnO nanorod film. The superior performance of the ZnO nanorod-based film is attributed to the paths for charge transport, which are directed towards the electrodes (Ravirajan *et al.*, 2006).

7.5 Relationship between material and device parameters and photovoltaic performance

In this section, we review the basic device physics of organic donor–acceptor solar cells and identify the key material and device parameters that should be addressed in order to improve power conversion efficiency.

7.5.1 Device physics of molecular heterojunction solar cells

As with all optoelectronic semiconductor devices, the current–voltage characteristics of an organic solar cell can be modelled using the continuity equations for each charge type. For electrons in the steady state we have

$$\frac{1}{q} \nabla \cdot i_n + g - r = 0 \quad (7.1)$$

where q is the magnitude of the electronic charge, g the volume generation rate of free electron–hole polaron pairs, r the charge-pair volume recombination rate and i_n the electron current density. Similarly for holes,

$$\frac{1}{q} \nabla \cdot i_p + g - r = 0 \quad (7.2)$$

where i_p is the hole current density. If the forms of g , r and $i_{n/p}$ are known in terms of the electron and hole polaron densities n and p , respectively, then eqs. 7.1 and 7.2 can be solved subject to appropriate boundary conditions at the interfaces and the electrodes. In molecular materials, where the dependence of g , r and i on charge density is non-trivial, these equations must usually be solved by numerical methods using appropriate expressions for each of g , r and i . In the case of bilayer devices, the equations can be solved by treating each layer as a separate one-dimensional domain. Numerical modelling of bilayer devices has been undertaken by several groups (Barker *et al.*, 2003; Gregg and Hanna, 2003; Peumans *et al.*, 2003b). To treat a bulk heterojunction structure correctly, an appropriate model of the morphology would be needed and the continuity equations would need to be solved in three dimensions within each domain, subject to boundary conditions at the interfaces. Such a problem is extremely challenging, and so far has only been tackled using Monte Carlo methods (Watkins *et al.*, 2005; Frost *et al.*, 2006). A much more practical approach is to treat the blend as an effective medium and consider variations in only one dimension, perpendicular to the planar electrodes. Then eq. 7.1 refers to electron polarons in the acceptor material and eq. 7.2 to hole polarons in the donor material, and the properties of the interface are parameterised into the coefficients of charge separation and recombination. As usual, the i - V characteristic is found by solving eqs. 7.1 and 7.2 subject to boundary conditions on i_n , n , i_p and p that depend on the applied potential V and the built-in potential difference between the device electrodes. Such one-dimensional effective-medium models have been used by several groups (Nelson, 2003; Koster *et al.*, 2005; Lalic and Inganas, 2005; Braun, 2007).

Calculation of the steady-state i - V characteristic is more complex for organic than for inorganic solar cells. In the case of a crystalline p - n junction device, g is simply related to the light-absorption profile and i and r are simple (often linear) functions of the carrier densities. In molecular materials, the dependence of g , r and i on carrier densities are non-trivial and not well known in many situations. We comment on each of the terms below.

Charge-generation term

This is given by $g = g_{ex}\eta_{ex}$, where g_{ex} is the exciton generation rate and η_{ex} the exciton dissociation probability. The position dependence of g_{ex} can be found by solving Maxwell's equations for light absorption in the thin, layered device structure. Because of the low thicknesses and low dielectric permittivity, absorption is strongly influenced by optical interference. In an effective medium, η_{ex} can be treated as a

uniform constant that depends on the intimacy of mixing. In a bilayer, this is a function that decreases exponentially with distance from the planar heterojunction.

Charge-transport term

In principle, i can be treated as the sum of diffusion and drift components, but we need to allow for the fact that disorder in transport energy levels leads to dispersion in the microscopic hopping rates and to charge trapping, which between them lead to diffusion constants and mobilities that are effectively charge-density-dependent. In addition, the Einstein relation between diffusion constant and mobility is unlikely to hold (Roichman and Tessler, 2002).

In a BHJ, when treated as an effective medium, electron and hole densities can co-exist everywhere and charge-density gradients are controlled only by the electrodes and by the charge-generation profile. In a planar bilayer, each phase contains only one type of charge carrier, and charge-density gradients are controlled by the donor–acceptor interface as well as by the charge-pair generation profile and the electrodes, so the $\nabla \cdot i$ term is more important. The drift term is often considered to be significant in organic devices; however, detailed models show that the internal electric field depends strongly upon the density of charges in the active region, including trapped charge, while the charge mobility also depends upon the density of filled traps. One way to approximate the effect of traps on charge transport in organic semiconductors is to let $\mu \sim n^\alpha$ where α is related to the energetic distribution of traps (Nelson, 2003).

Charge-recombination term

In the present context, r refers to the recombination of electrons and holes once separated and not to the non-dissociative decay of photogenerated excitons. In principle, recombination consists of two stages: the opposite charges must first come within a certain distance of each other from which they can interact, and then the interfacial charge transfer must occur. The first process is controlled by the size and location of the different material phases. For bilayer devices, charges which come within a certain distance of the donor–acceptor interface are liable to recombine. For a BHJ modelled as an effective medium, there is no simple, tested way to incorporate the probability of charges meeting. This has been modelled by several groups as a Langevin recombination process (Mihailetchi *et al.*, 2005; Pivrikas *et al.*, 2005), which would be appropriate for a continuous medium containing both charge types and with trap-free transport. The Langevin expression using measured mobilities will however overestimate recombination in a phase-segregated BHJ (and this is

confirmed by comparison with experiment (*e.g.* Pivrikas *et al.*, 2005), because the role of the different phases in protecting the different charge populations from each other is neglected). There is at present no satisfactory way of parameterising recombination rates for a phase-segregated medium into an effective recombination rate. Microscopic Monte Carlo modelling incorporating the effects of phase morphology and charge trapping is capable of reproducing experimental data (Nelson, 2003; Offermans *et al.*, 2003), but the application to a one-dimensional device model would require parameterisation of Monte Carlo results for a range of conditions.

A further aspect, not yet treated in detail for organic solar cells, is the role of intermediate charge-transfer states, such as bound polaron pairs, in mediating charge separation and recombination rates (Morteani *et al.*, 2004).

7.5.2 Goals for improved device performance

In spite of shortcomings, numerical modelling of organic device behaviour together with experimental observations has established the main areas in which molecular photovoltaic materials and devices need to be improved in order for the technology to become viable. We identify these areas in the context of the comparison of a typical high-efficiency silicon solar cell with the best molecular solar cells. Figure 7.9 shows the current–density voltage characteristics of the two types of device.

The short-circuit current density i_{sc} is much lower in the best organic photovoltaic devices ($i_{sc} \sim 10\text{--}12 \text{ mA cm}^{-2}$ compared with over 40 mA cm^{-2} for crystalline silicon). This is mainly due to: (i) the limited range of spectral sensitivity of molecular photovoltaic materials compared with inorganic semiconductors such as silicon; (ii) the limited optical depth, resulting from the low device thicknesses required to minimise recombination losses; (iii) failure to dissociate photogenerated excitons, as a result of unfavourable morphology (often a problem for new materials combinations); and (iv) slow charge transport, leading to recombination before collection at the interfaces.

Fill factors (FF) for organic devices are lower than for the best inorganic devices. Good organic solar cells may offer FF values of up to 0.6, compared with 0.75 for crystalline inorganic solar cells. One commonly proposed reason is the increased probability of recombination with increasing output voltage, resulting from slower transport relative to recombination with decreasing internal electric field (Schilinsky *et al.*, 2004); however, this explanation depends on the existence of a significant electric field at forward bias. Other likely reasons include series resistance due to low intrinsic charge mobilities and low electrode conductivity, and shunt losses due to imperfectly selective electrodes.

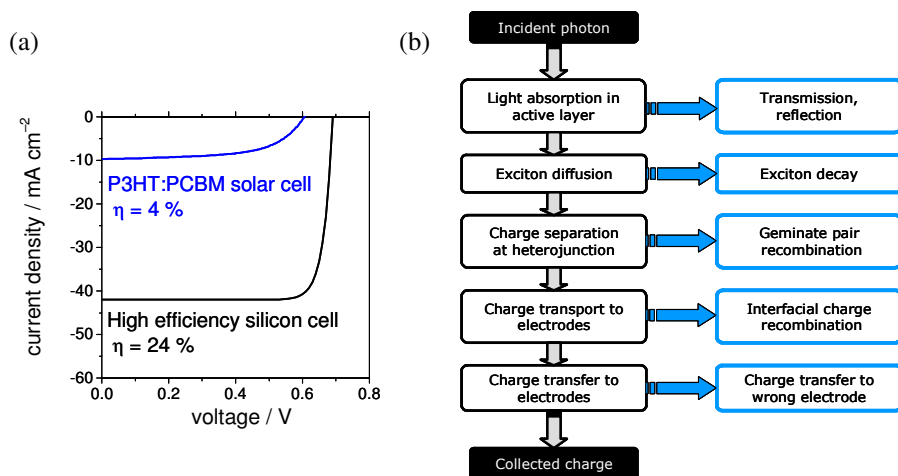


Figure 7.9 (a) Comparison of current density–voltage characteristics for a high-efficiency silicon solar cell and a state-of-the-art P3HT:PCBM bulk heterojunction solar cell. (b) Flow chart showing the main processes in an organic photovoltaic device. Blue arrows show undesirable loss processes, while grey arrows show the desired processes.

Finally, the open-circuit voltage V_{oc} is similar for organic and silicon PV devices (0.6–1.0 V compared with 0.7 V for crystalline silicon). However, for organic devices the difference between the energy of the lowest energy photons absorbed and qV_{oc} is large, ~ 1 eV for the best devices, while the equivalent difference is only about 0.4 eV in inorganic homojunctions. The factors controlling V_{oc} are reasonably well understood: consideration of the charge-separated state at the interface shows that qV_{oc} cannot be larger than the difference between the HOMO of the donor and the LUMO of the acceptor, *i.e.* $qV_{oc} < E_{HOMO,D} - E_{LUMO,A}$. Additionally, in a BHJ device with no significant asymmetry in the active layer, V_{oc} cannot be larger than the difference in work function between the two electrodes. Experimental studies and one-dimensional numerical modelling of BHJ devices have shown that thermal injection of charge carriers from electrodes into undoped organic layers leads to a bending of the energy levels close to the contacts, with the effect of reducing V_{oc} relative to its limiting value (Brabec *et al.*, 2001; Mihailetchi *et al.*, 2003; Mihailetchi *et al.*, 2004). In doped molecular heterojunctions, V_{oc} is limited by the difference in work functions of the *p*-type donor and *n*-type acceptor materials in a similar way as in an inorganic heterojunction. Perhaps the most interesting case is the undoped bilayer device, where V_{oc} is dominated by diffusion of charge carriers in opposite directions and the work functions of the electrodes do not need to be different to direct a photocurrent. In all

cases, the upper limit on qV_{oc} , assuming that charge separation requires the charge carriers to exist in different materials, is given by $E_{HOMO,D} - E_{LUMO,A}$. Since the optical gap is given by the lower of $(E_{HOMO,D} - E_{LUMO,D})$ and $(E_{HOMO,A} - E_{LUMO,A})$, the difference between V_{oc} and the optical gap is given by the interfacial HOMO or LUMO energy difference, *i.e.* by the driving force for charge separation. As mentioned above, the minimum driving force is estimated to be at least 0.3–0.6 eV (Halls *et al.*, 1999; Bredas *et al.*, 2004). However, in the best materials systems the actual value is much larger, *e.g.* ~ 1 eV in P3HT:PCBM devices. Therefore a clear goal is to identify material combinations offering a higher $(E_{HOMO,D} - E_{LUMO,A})$ difference without compromise to the optical absorption.

The primary factor limiting commercialisation of organic photovoltaics at present is low device durability. Organic solar cells suffer from instability in three main respects. First, many conjugated materials are unstable in the presence of oxygen and light. The photogenerated exciton is capable of reducing oxygen, generating reactive products that react with the molecular material and chemically degrade it. The second is the mechanical instability of donor–acceptor blends. After deposition, the components are frozen into a non-equilibrium configuration and the components may segregate over time, reducing the degree of blending and the effectiveness of charge separation. The latter is a particular problem with polymer:fullerene blends, where the fullerenes tend to cluster. Finally, the active-layer electrode interface can degrade over time, losing conductivity and increasing series resistance. Good encapsulation can make organic solar cells achieve the lifetimes required for some market applications, but in most cases this requires glass substrates or expensive multilayer barrier coatings. The use of glass significantly increases fabrication costs and weight, whilst limiting flexibility.

In the next sections, we review progress and approaches in six areas that are recognised as priorities for the improvement of organic solar cell performance.

7.6 Challenges

7.6.1 Increasing light absorption

A key focus of research into organic solar cells over the past decade has been the design of materials and devices to increase light absorption in the active layers. These efforts include the development of novel materials, the implementation of clever optics in the device structure to maximise the absorption of incident light, and new fabrication processes and surface modifications to maximise light harvesting.

A significant research effort has addressed the design and synthesis of new materials that absorb light at longer wavelengths than MDMO-PPV or P3HT. The highest theoretical efficiency for a single-junction cell is achieved for a band gap of 1.4 eV, which is much smaller than the optical gap of P3HT (1.9 eV). New red-absorbing conjugated polymers have been developed for this purpose, including polyfluorene block co-polymers that incorporate various thiophene and benzothio carbazole units into their structure (Perzon *et al.*, 2005), polythienylene vinylenes (Nguyen *et al.*, 2006) and donor–acceptor copolymers (Wienk *et al.*, 2006). BHJ solar cells made with polyfluorene polymers which have a broad absorption band from 800–1000 nm, blended with PCBM or other soluble fullerene derivatives, achieve power conversion efficiencies of up to 2.2% (Svensson *et al.*, 2003), which indicates that further material optimisation is necessary to improve the transport and charge-separation efficiencies.

Various alternative acceptor components for organic BHJ solar cells have been tried in an attempt to improve cell performance. Fullerene derivatives such as C₇₀:PCBM and C₈₄:PCBM have been used in place of C₆₀:PCBM, because the lower molecular symmetry compared with C₆₀:PCBM enables stronger light absorption by the fullerene. The C₇₀:PCBM derivatives were relatively successful, leading to 3% power conversion efficiency for devices made with MDMO-PPV polymer (Wienk *et al.*, 2003). The C₈₄ derivatives resulted in rather poor device efficiencies, attributed to the unfavourable film morphology resulting from the immiscibility of C₈₄ derivatives with typical organic solvents (Kooistra *et al.*, 2006).

Inorganic semiconductor nanoparticles have also been implemented as electron acceptors. For example, CdSe, CuInSe₂ and PbS have been of interest because they absorb in the visible and can extend the blend absorption out to the near infrared (Huynh *et al.*, 2002; Sun *et al.*, 2003), as discussed in Section 7.4.4. In one study, CdSe nanoparticles were combined with single-walled carbon nanotubes for improved light harvesting and as material variations for BHJ devices (Robel *et al.*, 2005).

Modification to the optical design of device structures has been a second area of rich activity. Here there are two goals: to harvest light that would otherwise be lost by transmission or reflection, and to manipulate light absorption so that excitons are more likely to be generated in the active layer. Optical models based on solution of Maxwell's equations have been developed by several groups for this purpose (Pettersson *et al.*, 1999; Peumans *et al.*, 2003b). In planar devices, the exciton generation peak can be shifted towards the donor–acceptor interface by controlling the thickness of wide optical-gap layers near the electrodes (Peumans *et al.*, 2000). In the case of BHJ devices, the effect of a TiO₂ cathode layer was attributed partly to optical effects (Kim *et al.*, 2006b). Larger effects on light harvesting could be

achieved, in principle, by using grating structures of period similar to the wavelength of light within the device. This has been studied experimentally by Inganas and co-workers using soft embossing to pattern the polymer layers (Roman *et al.*, 2000) and by Niggemann *et al.* (2004) using lithographically-produced nanostructured substrates. Despite theoretical predictions, such structures have not produced improved devices. Known problems include the effect of nanostructuring on electrode quality and exciton quenching close to the nanostructured metal.

A technologically simpler approach to light trapping is to include waveguides in the device structure below the anode of the solar cell (Zaban *et al.*, 2006). In such structures, light that is incident at large angles is channelled through the waveguide so that it can be absorbed by the active layer of the device. Any light that is transmitted through the active layer is reflected at the metal cathode back into the waveguide for a second chance at being absorbed. This process enhances long-wavelength light absorption in the device.

Variations in the structure of materials used for the active layer of solar cells can also significantly enhance the light-harvesting capabilities. For example, incorporation of (electronically inert) TiO₂ nanoparticles into an organic film has been shown to enhance light absorption (Kim *et al.*, 2003). In a very different approach, the specific donor–acceptor interactions can be exploited to enhance absorption. One group has shown that active layers made out of porphyrin dendrimers and fullerene dye units can form supramolecular clusters which absorb light over the entire range of the visible spectrum (Hasobe *et al.*, 2005). This indicates that the π – π interaction between the porphyrin units and fullerene components play a critical part in light absorption in the system.

A final promising technique used to improve the light harvesting in organic solar cells is to fabricate tandem solar cells with materials that absorb in different parts of the solar spectrum. Figure 7.10 shows the basic concept. In the two-terminal tandem device, short-wavelength light that is incident through the substrate of the device is absorbed in the blue-absorbing layer, or ‘top cell’ (1) while long-wavelength incident light is transmitted through (1) to be absorbed in the red-absorbing layer or ‘bottom cell’ (2). This improves the useful light collection in the device and greatly increases the open-circuit voltage because the individual ‘top’ and ‘bottom’ cell voltages are additive in this configuration. However, the current in this structure is limited by the lower current of the two junctions that make up the tandem cell, and the currents generated in the two parts of the device must be matched to allow efficient device performance.

In organic photovoltaics, tandem structures can be used to increase useful light absorption in a limited spectral range, rather than to extend the spectral range, and so

the top and bottom cells may be made from the same material. CuPc:C₆₀-based structures have led to efficiencies of 5.7% (Xue *et al.*, 2004b), and ZnPc:C₆₀ structures to efficiencies of 3.8% (Drechsel *et al.*, 2005). Tandem solar cells have also been fabricated for polymer-blend structures using a solution-processed technique (Hadipour *et al.*, 2006). Efforts continue to refine procedures to produce multilayer polymer structures by solution processing. If this could be achieved, tandem structures could significantly increase the efficiency of polymer-based BHJ devices.

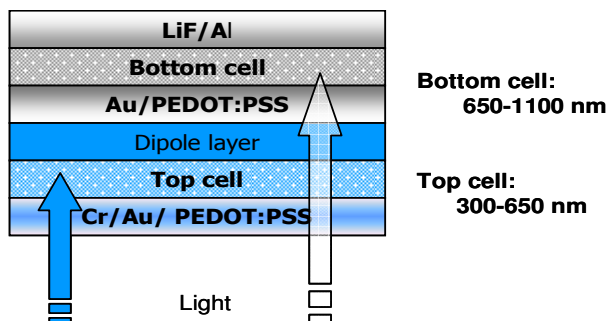


Figure 7.10 Tandem solar cell structure for polymer blend solar cells, based on the design demonstrated by Hadipour *et al.* (2006). In this all-solution-processed device, the top cell consists of a polymer:PCBM bulk heterojunction with an absorption maximum of 550 nm and preferentially absorbs short-wavelength light, while the bottom cell is made from a bulk heterojunction of PCBM with a red-absorbing polymer and absorbs longer-wavelength light. The composite gold-PEDOT:PSS internal layer connects the two cells in series.

7.6.2 Increasing the open-circuit voltage by control of interfacial energy levels

As explained above, an upper limit to the open-circuit voltage V_{oc} is given by the difference in energy of the donor HOMO level and the acceptor LUMO level. This difference is necessarily less than the optical gap of either material because of the energy-level offset necessary for charge separation, as shown in Fig. 7.11a. A relationship between qV_{oc} and $E_{HOMO,D} - E_{LUMO,A}$ was observed by Brabec *et al.* (2001) on varying the electron affinity of the electron-accepting material in MDMO-PPV: fullerene derivative blend devices, and by Scharber *et al.* (2006) on varying the ionisation potential of the polymer in polymer:PCBM devices (Fig. 7.11b). The latter study led to the conclusion that

$$qV_{oc} = E_{HOMO,D} - E_{LUMO,A} - 0.3 \text{ eV} \quad (7.3)$$

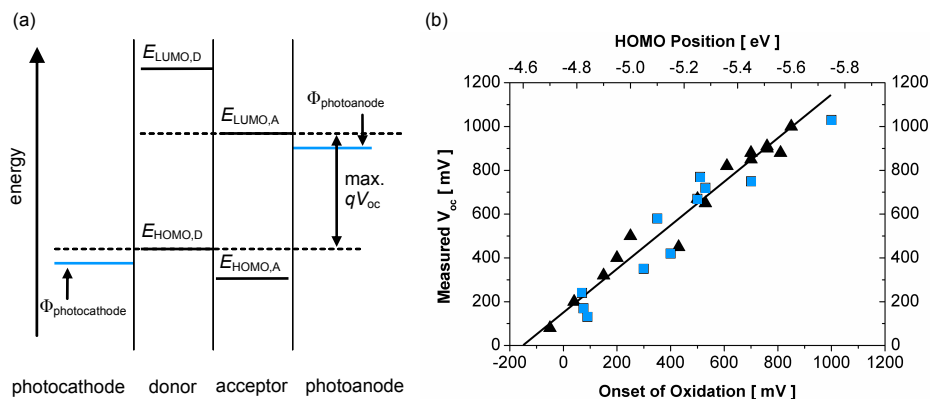


Figure 7.11 (a) Energy-level offsets for electron donors and acceptors in organic heterojunction solar cells. The upper limit to the open-circuit voltage is given by the energy difference between the HOMO of the donor and the LUMO of the acceptor. In the ideal situation, the work function $\Phi_{\text{photocathode}}$ of the hole-collecting electrode is well matched to the HOMO level of the donor, and the work function $\Phi_{\text{photoanode}}$ of the electron-collecting electrode is well matched to the LUMO level of the acceptor. (b) Experimental results showing the dependence of open-circuit voltage on the position of the HOMO level of the donor in polymer:PCBM bulk heterojunction solar cells, from Scharber *et al.* (2006). The black triangles denote polymers that are proprietary to Konarka, and the blue squares devices made from known chemicals as described by Sharber *et al.* (2006).

Calculations of limiting efficiency based on this relationship indicate that materials with optical gaps less than 1.74 eV and LUMO levels less than 3.92 eV below the vacuum level are needed in order to approach device efficiencies of 10% (Scharber *et al.*, 2006). This study indicates that the ionisation potential of the polymer is a determining factor in device performance, and progress depends on developing new materials with specific electrochemical properties. It should be noted that new electrode materials of very high or low work function will be needed to extract the high open-circuit voltage enabled, in principle, by such materials.

Related to the goal of optimising the interfacial energy-level alignment in order to increase V_{oc} , some fundamental research has focused on studies of materials with different energy-level configurations in an attempt to better understand the influence of the electrochemical properties of the materials on device performance. One such study showed not only that the ionisation potential of the polymer is critical for charge separation in polymer:PCBM bulk heterojunction solar cells, but also that the conditions that enable charge separation can also lead to formation of a charge-transfer complex between the donor and acceptor components of the blend (Benson-Smith *et al.*, 2007). Ground-state absorption, which may be due to such a charge-

transfer state, has been observed in several polymer:PCBM blends (Goris *et al.*, 2005; Goris *et al.*, 2006; Benson-Smith *et al.*, 2007). These observations may help to elucidate the role of intermediate excited states in charge separation and photovoltage generation. Further investigations of the correlations between material parameters, open-circuit voltage and charge separation are needed to clarify the factors controlling the open-circuit voltage. To understand the effect of material variations properly, it is also important to test a wide range of acceptor materials and determine their influence on device properties. While high-mobility electron acceptors are rare, many groups are working to synthesise new acceptors to be used for organic solar cell applications.

7.6.3 Improving charge transport

Charge mobilities in organic photovoltaic materials are typically at least three orders of magnitude lower than in crystalline inorganic semiconductors. Experiments have shown that low mobilities limit the charge-collection efficiency of organic solar cells. In the case of P3HT:PCBM, for example, the increase in short-circuit current resulting from increased regioregularity of the polymer material was attributed partly to increased charge mobilities (Kim *et al.*, 2006a), and mobility was correlated with device performance for a series of P3HT materials of different molecular weight (Ballantyne *et al.*, 2006). Modelling indicates that mobilities of up to $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ would be beneficial and would allow larger active-layer thicknesses (Braun, 2007). It is particularly important to balance the electron and hole mobilities so as to avoid electric field distortion through build up of space charge in the active layer. For this reason, several groups are working to produce materials and material combinations with fast and balanced transport for both holes and electrons. The following are some active research directions with this objective:

- *Polymers*: new polythiophene derivatives and analogues with hole mobilities at least as high as those in P3HT are being investigated (Heeney, 2007), as are other new high mobility polymers (Mulbacher *et al.*, 2006).
- *Discotic liquid crystals*: these offer extremely high mobilities as well as potential for self-organisation (Schmidt-Mende *et al.*, 2001; Andrienko *et al.*, 2006).
- *Polymer brushes*: the organised growth of polymers from sites on the surface of a substrate may lead to very good vertical transport due to structured vertical alignment of the polymer chains. This is discussed further in Section 7.6.4.
- *Carbon nanotubes*: these offer very high mobilities, but difficulties remain in fabricating devices without large shunt losses (Kymakis *et al.*, 2003).

Some of the most effective methods of improving charge transport in organic photovoltaics have used nanocrystalline inorganic materials as the electron acceptors. Sun *et al.* (2005) have successfully used CdSe tetrapods as electron acceptors with MDMO-PPV polymer in a solution-processed cell, with 2.1% power conversion efficiency under AM 1.5 conditions. Additionally, aligned CdTe nanorods (Kang *et al.*, 2005) and vertically aligned ZnO rods (Olson *et al.*, 2006; Ravirajan *et al.*, 2006) have been used with conjugated polymers as electron-accepting materials. These approaches have not yet resulted in efficiencies to exceed those of polymer: fullerene blend devices. However, high charge mobilities ($> 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) are essential for efficient organic solar cell operation.

7.6.4 Optimising morphology

Studies on BHJ structures have shown that morphology strongly influences device performance and that some degree of phase separation appears to be required for efficient operation. Theoretical considerations show that an ideal configuration would contain well-ordered, vertically aligned phases of each material in an interdigitated structure. Achieving a 'designer morphology' by solution processing is a formidable challenge. Nevertheless, this area of study is vital to the further understanding of BHJ devices and is a key research focus.

Processing conditions can greatly influence the self-assembly of polymer: small molecule blend films and thereby improve device efficiency. This is specifically true for P3HT:PCBM BHJ devices, where thermal annealing leads to crystallisation of both components. The resulting vertical and lateral restructuring of the film improves the absorption and photocurrent generation of the device (Kim *et al.*, 2005; Li *et al.*, 2005; Yang *et al.*, 2005). The degree of polymer crystallinity appears to be important in controlling this behaviour, and intensive research is being conducted to better understand this phenomenon and apply it to other material combinations.

The structure formed by donor: acceptor BHJ blends is dependent on the solvent used. Studies of polyfluorene: PCBM blends show that choice of solvent controls the segregation of materials within the blend film so that a vertical multilayer structure forms spontaneously in some cases (Bjorstrom and Moons, 2007). Similarly, the choice of solvent in a polymer-polymer blend controls the vertical arrangement of materials and the device performance (Arias *et al.*, 2002). Exploitation of these effects may open new avenues for materials-processing procedures in the organic photovoltaic field.

Efforts have been made to produce solution-processed, self-aligning films using a special class of materials called discotic liquid crystals. These flat, disc-like molecules preferentially stack in vertical columns and form clear pathways for charge transport in the solar cell. Early experiments yielded promising results in this area, with external quantum efficiencies of over 30%, but unfortunately the absorption range of the crystals was not suitably matched with the solar spectrum and thus the solar power conversion efficiencies achieved were limited (Schmidt-Mende *et al.*, 2001). New liquid-crystal materials are still being actively developed, on account of their high potential for use in organic photovoltaic devices.

A different approach is the block copolymer, where blocks of donor and acceptor moieties are attached to a polymer backbone. Self-organisation of the donor and acceptor units leads to donor and acceptor domain formation in a solid film, enabling domains of much smaller size than those that would spontaneously form in a blend (Lindner *et al.*, 2006). Figure 7.12 gives some examples of self-organising materials.

Taking a more radical approach to controlling morphology, studies have demonstrated the production of what are called ‘polymer brushes’ on conducting substrates. These polymers are grown vertically from the substrate using a surface-initiated polymerisation technique (Snaith *et al.*, 2005) and a layer of acceptor

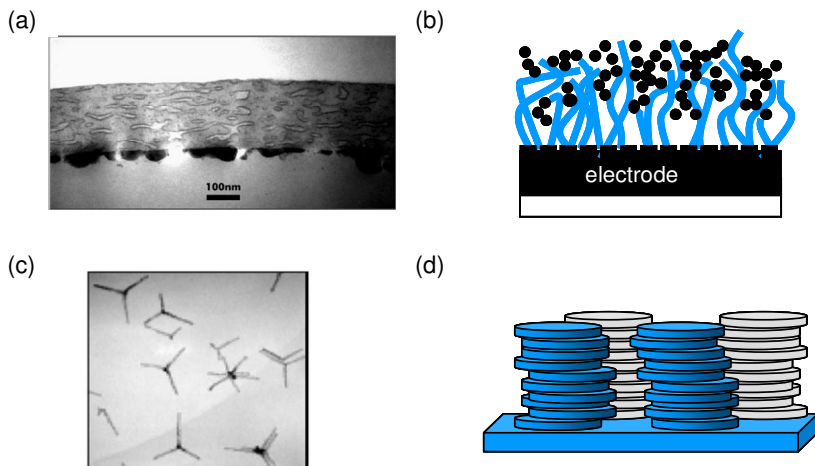


Figure 7.12 (a) Transmission electron microscope (TEM) image of a donor–acceptor block copolymer film. Domains formed are smaller than those achievable by blending two polymers (Lindner *et al.*, 2006); (b) Schematic of a polymer brush–nanoparticle heterojunction (Snaith *et al.*, 2005); (c) TEM image of CdSe tetrapods (Sun *et al.*, 2003); (d) Schematic of stacks of discotic liquid crystals. Fast charge transport along the stacks offers efficient charge collection, while columns of donor- and acceptor-type molecules in the same film could offer an optimum morphology for lateral charge separation.

material, such as CdSe nanoparticles, can be deposited on top of the polymer brushes to form a near-ideal bulk heterojunction film with interpenetrating networks of donor and acceptor materials and with a vertical composition gradient to help drive the photocurrent. The resulting photon-to-current quantum efficiencies reach up to 50%.

7.6.5 Improving electrodes

A number of approaches are being pursued to modify the electrodes in organic solar cells in order to improve conductivity, selectivity, stability or cost. These include new electrode materials, changes in device processing and additional electrode sub-layers. Most studies have been carried out using the leading material combination, P3HT:PCBM, as the active layer.

Alternative photocathode materials to ITO are sought because of the high cost and need for high-temperature fabrication of ITO, its imperfect selectivity and its limited chemical stability. To this end, new doped organic electrode layers such as new varieties of PEDOT:PSS with higher conductivity or higher stability than conventional PEDOT:PSS are being developed (Huang *et al.*, 2005). Sufficiently high conductivities in the doped organic layer could eliminate the need for ITO completely. Thin layers of carbon nanotubes (van de Lagemaat *et al.*, 2006) and fluorine-doped tin oxide (Yang and Forrest, 2006) have also been studied as lower-cost, hole-selective photocathode materials. As alternative electron collecting contacts, amorphous titanium dioxide has been successfully used as the top contact in a BHJ device, apparently with some advantage to optical confinement as well as charge collection (Kim *et al.*, 2006b).

Electrode selectivity can be improved, in principle, by inverting the layer structure: Waldauf *et al.* (2007) coat the ITO bottom contact with a layer of TiO₂, a highly selective electron-collecting material, and use PEDOT as a top contact to minimise shunt losses. Inverted structures that do not require ITO and are amenable to mass production have been developed (Glatthaar *et al.*, 2005) and offer efficiencies equal to conventional devices. The work function, and hence selectivity, of electrode materials can also be modified by applying additional layers, such as monolayers of permanent dipole-moment molecules (Khodabakhsh *et al.*, 2006), or interfacial layers of inorganic compounds. Differential doping of the organic layers is routinely used in vacuum-deposited molecular film devices, but is not yet straightforward with polymer-based devices.

An alternative strategy to achieve electrode selectivity is through control of the vertical distribution of the active layer. Coating of the photoanode preferentially with

the electron acceptor, and of the photocathode with the hole-transport material, prevents direct contact of either electrode with the wrong material and eliminates shunt paths, as shown in Fig. 7.13. This can be done deliberately using multilayer photoactive structures: studies have already shown that such built-in asymmetry leads to larger V_{oc} values (Snaith *et al.*, 2004). Such multilayer structures with electron-(hole-)blocking layers next to the photocathode (photoanode) can be fabricated by exploiting the different solubility of different organic materials. An alternative route to vertical segregation is to rely on the self-organisation of components within the active layer. Recent studies on P3HT : PCBM blends using spectroscopic ellipsometry have shown that vertical segregation within the blend occurs on annealing, and that the direction of segregation is driven by the nature of the contact materials, specifically by the relative surface energies between each component and the substrate relative to air (Campoy-Quiles *et al.*, 2007). This process can be controlled by varying the annealing conditions, type of substrate and top contact and applying interfacial layers.

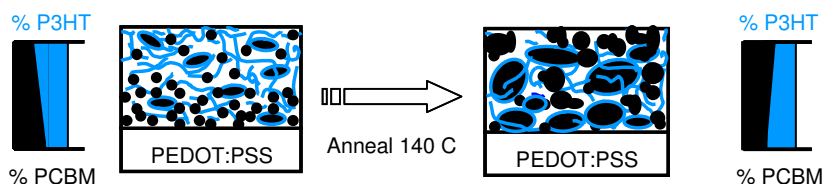


Figure 7.13 Schematic showing of segregation of P3HT (blue) and PCBM (black) phases during annealing above the glass-transition temperature of the polymer in a P3HT:PCBM blend film. On annealing, both phases crystallise and segregate vertically in a direction that is controlled by the nature of the substrate. Improved device performance results when the P3HT segregates towards the photocathode (PEDOT:PSS in this case) and PCBM towards the photoanode.

7.6.6 Improving device stability

We identify three types of degradation in organic photovoltaic devices: (i) photo-oxidation of the organic solid, leading to loss in conjugation and irreversible deterioration of the light-absorbing or charge-transporting properties; (ii) degradation of the conductive properties of the interfaces of the organic device; and (iii) mechanical disintegration, *e.g.* by the segregation over time of the donor and acceptor components in a bulk heterojunction structure. Despite its industrial importance, the photodegradation of organic solar cells has received little attention to

date. The few existing studies of organic solar cell stability have focussed on blends of conjugated polymers (typically MDMO-PPV) with fullerenes (usually PCBM) and have demonstrated the negative effect of photo-oxidation on the device performance, with loss of photocurrent within approximately one day under solar illumination (Neugebauer *et al.*, 2000; Kroon *et al.*, 2002; Jeranko *et al.*, 2004; Krebs *et al.*, 2004; Schuller *et al.*, 2004; Pacios *et al.*, 2006). These studies have shown that loss in short-circuit current density is the primary reason for the loss in power conversion efficiency, while the open-circuit voltage remains almost unchanged. Detailed studies indicate that the loss in photocurrent is partly due to degradation of charge-transport characteristics and only partly due to loss in optical absorbance (Pacios *et al.*, 2006). Photodegradation is slowed by encapsulation or by operation in inert atmospheres and aluminium top electrodes also appear to have a protective effect (Jeranko *et al.*, 2004; Krebs *et al.*, 2004). Separate studies have shown that photodegradation of a PPV derivative is slowed by the addition of the fullerene electron acceptor C₆₀ (Sarkas *et al.*, 1996; Neugebauer *et al.*, 2000). This effect can be attributed to photoinduced electron transfer to the acceptor occurring on a faster time scale than singlet–triplet intersystem crossing, so that triplet excitons, which may assist the photo-oxidation of PPV polymers, are not formed.

As yet there is no general solution to the problem of the photostability of conjugated solids. In the immediate term, devices must be encapsulated using glass or impermeable multi-layer organic–inorganic coatings (Weaver *et al.*, 2002). Organic solar cells encapsulated under glass achieve lifetimes of thousands of hours (Schuller *et al.*, 2004), and lifetimes comparable to those achieved by encapsulated organic light-emitting devices are feasible. In the long term, the most promising option is the design and development of more stable photoactive materials, once the fundamental mechanism and its relationship to chemical structure is sufficiently well understood.

Degradation of interface properties can in principle be addressed by modifying electrode materials or electrode interfaces. A recent study (Kawano *et al.*, 2006) showed that water-induced degradation of the interface between the PEDOT:PSS electrode and the active layer in a polymer–fullerene bulk heterojunction device leads to rapid deterioration of performance even in the dark. Such problems can be prevented by using alternative high work-function electrode materials or by developing less hygroscopic forms of PEDOT:PSS. Additionally, there has been some evidence that the stability of P3HT:PCBM devices is substantially enhanced when a TiO₂ layer is used as a hole-blocking layer.

Structural instability due to phase segregation in donor–acceptor blends over time is a function of materials and temperature. At moderate temperatures of 50–80 °C, the problem is more severe in MDMO-PPV:PCBM than P3HT:PCBM blend films. This

can be explained by the relatively low glass-transition temperature in MDMO-PPV, enabling rapid diffusion of fullerenes between the polymer chains. Replacing the polymer with a similar PPV derivative of higher glass transition temperature greatly slows down the degradation of both devices and blend morphology (Bertho *et al.*, 2007). Alternative approaches make use of cross-linking of organic components to ensure rigidity (Drees *et al.*, 2005). Thus, mechanical disintegration may be minimised by choice of active materials, solvent and electrodes, as well as by control of operating conditions. A separate means to avoid mechanical disintegration is to use rigidly connected porous templates such as inorganic semiconductor or metal oxide nanostructures, discussed in Section 7.4 above.

7.7 Summary

Organic semiconductors are attracting interest as photovoltaic materials because of the potential for low-cost device manufacture using solution processing. Because of the nature of intermolecular interactions in molecular solids, excitons produced by photoexcitation do not spontaneously produce separated charges, as they do in conventional semiconductor materials. However, an interface between two organic semiconductors of different electron affinity is capable of causing exciton dissociation to produce separate charges. Organic photovoltaic device designs include bilayer structures, consisting of thin planar layers of an electron-accepting and an electron-donating organic semiconductor, and three-dimensional blend films of the two materials, known as bulk heterojunctions. In both cases, charge separation occurs at the interface and is followed by electron transport through the electron acceptor and hole transport through the electron donor, towards the electrodes. The leading bilayer structures are made from vacuum-deposited molecular layers of metal phthalocyanines and fullerenes, and lead to power conversion efficiencies of 5%, while the leading bulk heterojunction structures are made from polythiophene polymer blends with soluble fullerene derivatives, and have reached power conversion efficiencies of 4–5%. The main obstacles to commercialisation of the technologies are the low efficiencies and poor device stability. Efficiency is limited mainly by the poor sensitivity of available organic semiconductors to red light, but also by low charge mobilities, by the loss of potential energy in the charge-separation process, and by imperfect device structures. Current research efforts aim to improve performance by development of new materials with extended spectral sensitivity, with optimised electronic energy levels, or with improved charge-transport properties; by optimisation of device architecture and electrode materials; and by optimisation of the

morphology of bulk heterojunction films through control of processing conditions and by exploiting the self-organising properties of a range of new materials. These developments are supported by ongoing improvement in understanding of the physics of organic photovoltaic devices. Power conversion efficiencies approaching 10% are considered to be achievable. Long-term device stability will require development of new photoactive and electrode materials and a more through understanding of the relationship between materials properties and degradation mechanisms.

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CHAPTER 8

DYE-SENSITISED MESOSCOPIC SOLAR CELLS

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On the arid lands there will spring up industrial colonies without smoke and without smoke-stacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in a distant future the supply of coal becomes completely exhausted, civilisation will not be checked by that, for life and civilisation will continue as long as the Sun shines!

Giacomo Ciamician, *Eighth International Congress of Applied Chemistry*,
Washington and New York, September 1912.

8.1 Introduction

Photovoltaic devices are based on charge separation at an interface of two materials of different conduction mechanism. To date this field has been dominated by solid-state junction devices, usually made of silicon, and profiting from the experience and material availability resulting from the semiconductor industry. The dominance of the photovoltaic field by inorganic solid-state junction devices is now being challenged by the emergence of a range of new device concepts, including devices based on nanocrystalline and conducting polymer films. These devices offer the prospect of very low-cost fabrication and present a range of attractive features that will facilitate market entry. It is now possible to depart completely from the classical solid-state junction device by replacing the phase contacting the semiconductor by an electrolyte,

liquid, gel or solid, thereby forming a photoelectrochemical cell. The phenomenal progress realised recently in the fabrication and characterisation of nanocrystalline materials has opened up vast new opportunities for these systems. Contrary to expectation, devices based on interpenetrating networks of mesoscopic semiconductors have shown strikingly high conversion efficiencies, competing with those of conventional devices. The prototype of this family of devices is the dye-sensitised solar cell (DSSC), which realises the optical absorption and charge-separation processes by the association of a sensitizer as light-absorbing material with a wide-bandgap semiconductor of nanocrystalline morphology (O'Regan and Grätzel, 1991).

8.2 Historical background

The history of the sensitisation of semiconductors to light of wavelength longer than that corresponding to the semiconductor bandgap has been presented elsewhere (McEvoy and Grätzel, 1994; Hagfeldt and Grätzel, 2000). It represents an interesting convergence of photography and photoelectrochemistry, both of which rely on photoinduced charge separation at a liquid–solid interface. The silver halides used in photography have bandgaps of the order of 2.7–3.2 eV, and are therefore insensitive to much of the visible spectrum, as are the metal oxide films now used in dye-sensitised solar cells.

The first panchromatic film able to render the image of a scene realistically into black and white followed on the work of Vogel in Berlin after 1873 (West, 1874), in which he associated dyes with the halide semiconductor grains. The first sensitisation of a photoelectrode followed shortly thereafter, using similar chemistry (Moser, 1887). However, the clear recognition of the parallels between the two procedures—realisation that the same dyes can in principle function in both systems (Namba and Hishiki, 1965) and verification that their operating mechanism is by injection of electrons from photoexcited dye molecules into the conduction band of the *n*-type semiconductor substrates (Gerischer and Tributsch, 1968)—dates only to the 1960s. In the years that followed it became recognised that the dye could function most efficiently if chemisorbed on the surface of the semiconductor (Tsubomura *et al.*, 1976; Anderson *et al.*, 1979; Dare-Edwards *et al.*, 1980). The concept of using dispersed particles to provide a sufficient interface area then emerged (Dung *et al.*, 1984), and was subsequently employed for photoelectrodes (Desilvestro *et al.*, 1985).

Titanium dioxide (TiO₂) quickly became the semiconductor of choice for the photoelectrode on account of its many advantages for sensitised photochemistry and photoelectron chemistry: it is a low-cost, widely available, non-toxic and bio-

compatible material, and as such is even used in healthcare products as well as industrial applications such as paint pigmentation. Initial studies of the TiO_2 -based DSSC employed tris-bipyridyl ruthenium(II) dyes, which are paradigm sensitiser for photochemical studies, functionalised by the addition of carboxylate groups to attach the chromophore to the oxide substrate by chemisorption. Progress thereafter was incremental, a synergy of structure, substrate roughness and morphology, dye photophysics and electrolyte redox chemistry, until the announcement in 1991 (O'Regan and Grätzel, 1991) of a sensitised electrochemical photovoltaic device with an energy conversion efficiency of 7.1% under solar illumination. That evolution has continued progressively since then, with certified efficiencies now over 11%.

8.3 Mode of function of dye-sensitised solar cells

8.3.1 Device configuration

Figure 8.1 is a schematic of the components of a DSSC. At the heart of the system is a mesoporous oxide layer composed of nanometre-sized particles that have been sintered together to allow electronic conduction to take place. The material of choice has been TiO_2 (anatase) although alternative wide-gap oxides such as ZnO , SnO_2 and Nb_2O_5 have also been investigated (Hoyer and Weller, 1995; Ferrere *et al.*, 1997; Rensmo *et al.*, 1997; Sayama *et al.*, 1998; Green *et al.*, 2005). Attached to the surface of the nanocrystalline film is a monolayer of a sensitiser dye. Photoexcitation of the latter results in the injection of an electron into the conduction band of the oxide, generating the dye cation. The original state of the dye is subsequently restored by electron donation from the electrolyte; this step is often referred to as the regeneration reaction. The electrolyte usually comprises an iodide/triiodide redox couple dissolved in a liquid organic solvent, although attention is increasingly focusing on alternatives for the solvent, including ionic liquids, gelled electrolytes and polymer electrolytes (Stathatos *et al.*, 2003; Wang *et al.*, 2003b; Nogueira *et al.*, 2004; Durr *et al.*, 2005). The regeneration of the sensitiser by iodide intercepts the recapture of the injected electron by the oxidised dye. The iodide is in turn regenerated by the reduction of triiodide at the counter electrode, with the electrical circuit being completed via electron migration through the external load.

The high surface area of the mesoporous metal oxide film is critical to efficient device performance as it allows strong absorption of solar irradiation to be achieved by only a monolayer of adsorbed sensitiser dye. Whereas a dye monolayer absorbed on a flat interface exhibits only negligible light absorption (the optical absorption

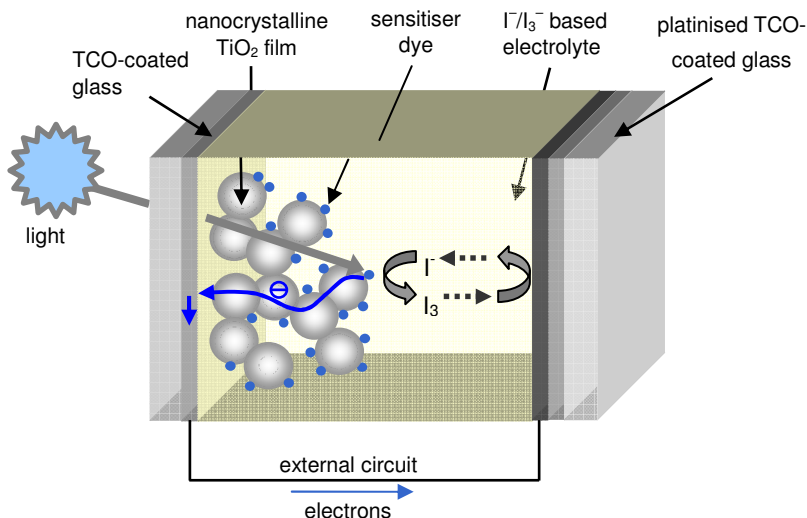


Figure 8.1 Schematic of a liquid electrolyte dye-sensitised solar cell. Photoexcitation of the sensitiser dye is followed by electron injection into the conduction band of the mesoporous oxide semiconductor, and electron transport through the metal oxide film to the TCO-coated glass working electrode. The dye molecule is regenerated by the redox system, which is itself regenerated at the platinumised counter electrode by electrons passed through the external circuit.

cross-sectional areas for molecular dyes being typically 2–3 orders of magnitude smaller than their physical cross-sections), the use of a mesoporous film dramatically enhances the interfacial surface area over the geometric surface area, by up to a 1000-fold for a 10 μm thick film, leading to high visible-light absorbance from the many successive monolayers of adsorbed dye in the optical path. Another advantage of the use of a dye monolayer is that there is no requirement for exciton diffusion to the dye/metal oxide interface, and also the non-radiative quenching of excited states often associated with thicker molecular films is avoided. The high surface area of such mesoporous films does however have a significant downside, as it also enhances interfacial charge-recombination losses, a topic we return to in more detail below.

A recent alternative embodiment of the DSSC concept is the replacement of the redox electrolyte with a solid-state hole conductor, which may be either inorganic (Tennakone *et al.*, 1995; O'Regan and Schwartz, 1998) or organic (Bach *et al.*, 1998), thereby avoiding the use of a redox electrolyte. Such solid-state sensitised heterojunctions can be regarded as functionally intermediate between redox electrolyte-based photoelectrochemical DSSCs and the organic bulk heterojunctions described in

Chapter 7. Devices efficiencies for such solid-state DSSCs are as yet limited to ~4% (Snaith *et al.*, 2005), in contrast to efficiencies of over 11% achieved for the more widely studied redox electrolyte-based DSSCs (Chiba *et al.*, 2006).

8.3.2 Device fabrication

DSSCs are typically fabricated on transparent conducting oxide (TCO) glass substrates, enabling light irradiance through this substrate under photovoltaic operation. The conductive coating typically used is fluorine-doped SnO_2 (FTO), preferred over its indium-doped analogue (ITO) for reasons of lower cost and enhanced stability. Prior to deposition of the mesoporous TiO_2 film, a dense TiO_2 film may be deposited to act as a hole blocking layer, preventing recombination (shunt resistance) losses between electrons in the FTO and oxidised redox couple.

The TiO_2 nanoparticles are typically fabricated by the aqueous hydrolysis of titanium alkoxide precursors, followed by autoclaving at temperatures up to 240 C to achieved the desired nanoparticle dimensions and crystallinity (anatase) (Barbe *et al.*, 1997). The nanoparticles are deposited as a colloidal suspension by screen printing or by spreading with a doctor blade, followed by sintering at ~450 C to ensure good interparticle connectivity. The film porosity is controlled by the addition of an organic filler such as carbowax to the suspension prior to deposition; this filler is subsequently burnt off during the sintering step. Figure 8.2 shows a scanning electron micrograph of a typical mesoporous TiO_2 film. Typical film thicknesses are 5–20 μm , with TiO_2 mass 1–4 mg cm^{-2} , film porosity 50–65%, average pore size 15 nm and particle diameter 15–20 nm.

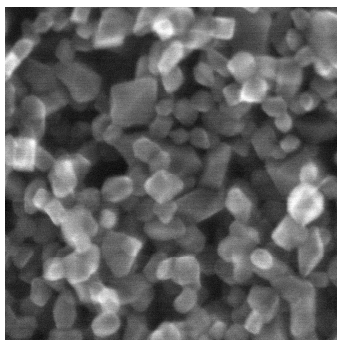


Figure 8.2 Scanning electron micrograph of a typical mesoscopic TiO_2 film employed in DSSCs. Note the bipyramidal shape of the particles, with (101) oriented facets exposed. The average particle size is 20 nm.

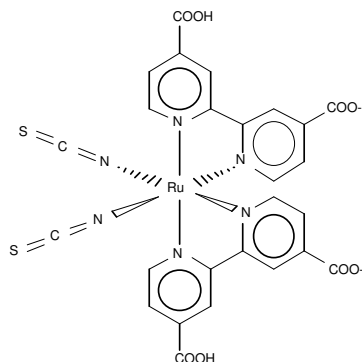


Figure 8.3 Chemical structure of the N719 ruthenium complex used as a charge-transfer sensitiser in dye-sensitised solar cells. The N3 dye has the same structure, except that all four carboxylates are protonated.

The classic sensitiser dye employed in DSSCs is a ruthenium (II) bipyridyl dye, *cis*-bis(isothiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II), which is usually referred to as 'N3', or in its partially deprotonated form (a di-tetra butylammonium salt) as 'N719' (Nazeeruddin *et al.*, 1993). Figure 8.3 shows the structure of this dye. The incorporation of carboxylate groups allows ligation to the film surface via the formation of bidendate and ester linkages, whilst the (–NCS) groups enhance the absorption of visible light. Adsorption of the dye to the mesoporous film is achieved by simple immersion of the TiO_2 film in a solution of dye, which results in the conformal adsorption of a dye monolayer to the film surface. The counter electrode is fabricated from FTO-coated glass, with the addition of a Pt catalyst to catalyse the reduction of the redox electrolyte at this electrode. Electrical contact between working and counter electrodes is achieved by the redox electrolyte, with capillary forces being sufficient to ensure the electrolyte efficiently penetrates the film pores.

8.3.3 Energetics of operation

Figure 8.4 illustrates the energetics of DSSC operation. In contrast to silicon and organic devices, the high concentration (~ 0.5 M) of mobile ions in the electrolyte effectively screens out any macroscopic electric fields. Charge separation is therefore primarily driven by the inherent energetics (oxidation/reduction potentials) of the different species at the TiO_2 /dye/electrolyte interface rather than by the presence of macroscopic electrostatic potential energy gradients. Similarly, charge-transport

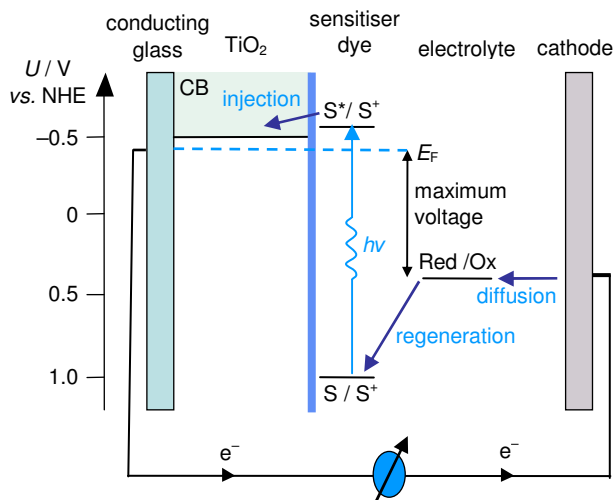


Figure 8.4 Energetics of operation of DSSCs. The primary free energy losses are associated with electron injection from the excited sensitizer into the TiO_2 conduction band and regeneration of the dye by the redox couple. The voltage output of the device is approximately given by the splitting between the TiO_2 Fermi level (dashed line) and the chemical potential of the redox electrolyte.

processes are primarily diffusive, driven by concentration gradients in the device generated by the photoinduced charge separation. Photoinduced charge separation occurs at the dye-sensitized TiO_2 /electrolyte interface. Electron injection requires the dye excited state to be more reducing than the TiO_2 conduction band, enabling transfer of an electron from photoexcited dye into the metal oxide. This energetic requirement is equivalent to the dye excited-state LUMO orbital having a lower electron affinity than the electrode conduction-band edge. Similarly, regeneration of the dye ground state by the redox couple requires the dye cation to be more oxidising than the iodide/triiodide redox couple. Charge separation in DSSCs can be regarded as a two-step redox cascade, resulting in the injection of electrons into the TiO_2 electrode and the concomitant oxidation of the redox electrolyte. Figure 8.4 shows typical values for the interfacial energetics in DSSCs. Both charge-separation reactions are thermodynamically downhill and can be achieved with near unity quantum efficiency in efficient devices.

Following charge separation, charge collection from the device requires transport of the photogenerated charges to their respective electrodes. For an efficient DSSC under AM1.5 solar irradiance, these charge fluxes are of the order of 20 mA cm^{-2} . The high ionic concentrations in the device effectively screen out any macroscopic

electric fields, thereby removing any significant drift component of these transport processes. The transport of both electrons and redox ions are therefore both primarily driven by diffusion processes resulting from concentration gradients. Under optimum conditions (*e.g.* good TiO_2 nanoparticle interconnections and a low-viscosity electrolyte), these charge-transport processes (electrons towards the FTO working electrode, triiodide towards the counter electrode) can be efficiently driven with only modest concentration gradients, and therefore only small free energy losses (<50 meV). At the counter electrode, the triiodide is re-reduced back to iodide, the platinum catalyst enabling this reaction to proceed with minimal overpotential (again <50 meV). A similarly ohmic contact is achieved at the TiO_2 /FTO interface. It is apparent that the energetics at the TiO_2 /dye/electrolyte interface are of primary importance in determining the overall device energetics.

Power output from the DSSC requires not only efficient charge collection by the electrodes but the generation of a photovoltage, corresponding to a free energy difference between the working and counter electrodes. In the dark at equilibrium, the Fermi energy of the TiO_2 electrode (corresponding to the free energy of electrons in this film after thermalisation) equilibrates with the mid-point potential of the redox couple, resulting in zero output voltage. Under these conditions, the TiO_2 Fermi level lies deep within the bandgap of the semiconductor, and the film is effectively insulating, with a negligible electron density in the TiO_2 conduction band. Photo-excitation results in electron injection into the TiO_2 conduction band and concomitant hole injection into (oxidation of) the redox electrolyte. The high concentrations of oxidised and reduced redox couple present in the electrolyte in the dark mean that this photooxidation process does not result in a significant change in chemical potential of the electrolyte, which remains effectively fixed at its dark, resting value. In contrast, electron injection into the TiO_2 conduction band results a dramatic increase in electron density (from the order of 10^{13} cm^{-3} to 10^{18} cm^{-3}), raising the TiO_2 Fermi level towards the conduction-band edge, as illustrated in Fig. 8.4, and allowing the film to become conducting. This shift of the TiO_2 Fermi level under irradiation increases the free energy of injected electrons and is responsible for the generation of the photovoltage in the external circuit.

The mid-point potential of the redox couple is given by the Nernst equation, and is therefore dependent on the relative concentrations of iodide and iodine. The concentrations of these species required for efficient device function are in turn constrained by kinetic requirements of dye regeneration at the working electrode, and iodide regeneration at the counter electrode, as discussed below. Typical concentrations of these species are in the range 0.1–0.7 M iodide and 10–200 mM iodine, constraining the mid-point potential of this electrolyte to ~ 0.4 V *vs.* NHE. It should

furthermore be noted that in the presence of excess iodide, the iodine is primarily present in the form I_3^- , resulting in this electrolyte often being referred to as an iodide/triiodide redox couple.

Determining the energetics of the TiO_2 conduction band is more complex. As with most oxides, the surface of TiO_2 may be more or less protonated depending on the pH of the surrounding medium. The resultant changes in surface charge cause the surface potential to exhibit a nernstian dependence on effective pH, shifting by 60 mV per pH unit (Rothenberger *et al.*, 1992). In bulk metal oxides, surface charge can result in significant bending of the conduction and valence bands adjacent to the surface. However, in the mesoporous TiO_2 films employed in DSSCs, the nanoparticles are too small to support significant band bending. As a consequence, the whole conduction band of such mesoporous films shifts with the surface potential. At pH 1 in aqueous solutions, the conduction band edge for TiO_2 has been reported at -0.5 V vs. NHE, shifting negatively as the pH is increased (Hengerer *et al.*, 2000). DSSCs typically employ organic rather than aqueous electrolytes, complicating quantification of the effective pH. Nevertheless studies in organic solvents have demonstrated shifts of the conduction band of mesoporous TiO_2 films of up to 1 V depending on the concentration of potential-determining ions (primarily small cations such as protons or lithium cations) in the electrolyte (Redmond and Fitzmaurice, 1993). For this reason, the concentration of such potential-determining ions in the electrolyte plays a key role in determining the energetics of the dye-sensitised interface, and thereby device performance. Additives added to the electrolyte to determine such energetics include Li^+ , guanadinium ions, N-methylbenzimidazol and *t*-butyl pyridine (which functions as a base). Further influence on these interfacial energetics can be achieved by variation of the extent of protonation of the sensitiser dye.

The choice of suitable sensitiser dye energetics is essential to achieve suitable matching to the metal oxide and redox couple. The excited-state oxidation potential ($U_m(S^+/S^*)$) must be sufficiently negative to achieve efficient electron injection into the TiO_2 conduction band, whilst the ground-state oxidation potential must be sufficiently positive to oxidise the redox couple. The redox properties of adsorbed sensitiser dyes may differ significantly from those measured in solution, mainly due to the high surface-charge densities and dipoles, present at this interface (Zaban *et al.*, 1998). Notwithstanding this, typical dye redox energies empirically found to be compatible with efficient device function are $U_m(S^+/S) > 0.6$ V vs. NHE.

8.3.4 Kinetics of operation

Figure 8.5 is a photochemical view of the function of a DSSC, illustrating the sequence of electron transfer and charge-transport processes which result in photovoltaic device function. In addition to the forward electron transfer and transport processes, this figure also illustrates several competing loss pathways, shown as blue arrows. These loss pathways include decay of the dye excited state to ground, and charge recombination of injected electrons with dye cations and with the redox couple. Each charge-transfer step results in an increased spatial separation of electrons and holes, increasing the lifetime of the charge-separated state, but at the expense of reducing the free energy stored in this state. This functionality exhibits a close parallel to function of photosynthetic reaction centres. As in natural photosynthesis, kinetic competitions between the various forward and loss pathways are critical to determining the quantum efficiencies of charge separation and collection, and are therefore key factors determining energy conversion efficiency.

The theory of interfacial electron transfer, and the dependence of electron-transfer rate on interfacial energetics, are addressed in Chapter 4 of this book, and the

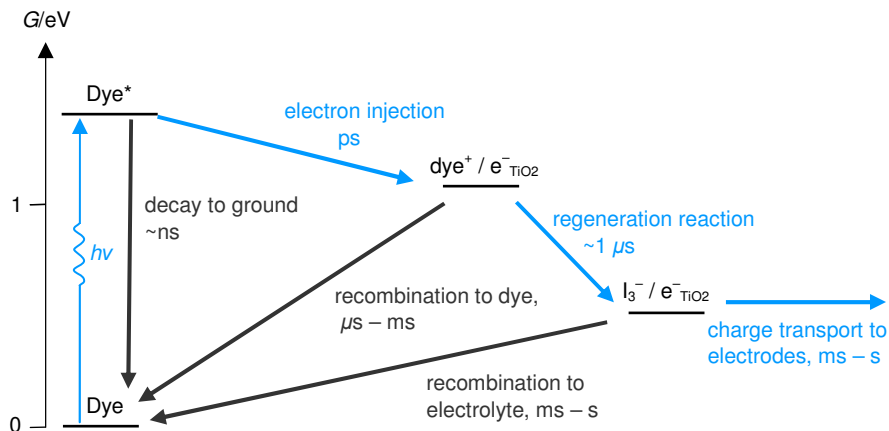


Figure 8.5 State diagram representation of the kinetics of DSSC function. Forward processes of light absorption, electron injection, dye regeneration and charge transport are indicated by blue arrows. The competing loss pathways of excited-state decay to ground and electron recombination with dye cations and oxidised redox couple are shown in grey. The vertical scale corresponds to the free energy G stored in the charge-separated states. Note the free energy of injected electrons is determined by the Fermi level of the TiO₂; the figure is drawn assuming a TiO₂ Fermi level 0.6 V above the chemical potential of the redox electrolyte (corresponding to a cell voltage of ~ 0.6 V, close to the maximum power point of typical DSSCs).

dynamics of charge transport in mesoscopic electrodes are addressed in Chapter 11. In this chapter we will therefore confine ourselves only to consideration of the impact of these dynamics on the performance of DSSCs.

Efficient electron injection requires the rate of electron injection to exceed excited-state decay to ground. Typical rates of dye excited-state decay to ground are in the range 10^7 – 10^{10} s⁻¹. The rate of electron injection depends on the electronic coupling between the dye excited-state LUMO orbital and accepting states in the TiO₂, and on the relative energetics of these states. In model system studies of dye-sensitised metal oxide films, electron injection rates of $>10^{12}$ s⁻¹ have been reported for a range of sensitiser dyes, consistent with efficient electron injection (Anderson and Lian, 2005; Durrant *et al.*, 2006). However it should be noted that fast electron injection dynamics require both strong electronic coupling of the dye LUMO orbital to the metal oxide conduction-band states, and a sufficient free energy difference to drive the reaction. As such, electron-injection dynamics are dependent on the energetics of the TiO₂ conduction band, and therefore on the concentration of potential-determining ions (*e.g.* Li⁺) in the electrolyte. Omission of such ions from the electrolyte can result in an insufficient energetic driving force, reducing the quantum yield of charge injection, and thereby reducing device photocurrent.

It should be noted that the heavy metal ion in the ruthenium bipyridyl dyes widely employed in DSSCs results in ultrafast (up to 10^{13} s⁻¹) intersystem crossing from the initially formed singlet excited state to a triplet state. This relaxation process reduces the excited-state free energy by ~400 meV. While several studies have reported sub-picosecond electron injection from the singlet excited state of these dyes, electron injection from the triplet state is significantly slower (10^{10} – 10^{11} s⁻¹), consistent with the lower free energy of this excited state, but still fast compared with decay of the triplet state to ground (10^7 – 10^8 s⁻¹) (Anderson and Lian, 2005; Durrant *et al.*, 2006). Recent studies of complete devices have suggested that this relatively slow electron injection from the dye triplet state may be the dominating injection pathway in efficient DSSCs (Haque *et al.*, 2005).

Efficient dye regeneration requires the rate of re-reduction of the dye cation by the redox couple to exceed that of charge recombination of injected electrons with these dye cations. This recombination reaction has been shown to be strongly dependent on the electron density in the TiO₂ electrode (and therefore light intensity and cell voltage), accelerating by at least an order of magnitude between short-circuit and open-circuit conditions (Durrant *et al.*, 2006). It is furthermore dependent on the spatial separation of the dye cation (HOMO) orbital from the metal oxide surface, with the rate constant decaying exponentially with distance, consistent with electron tunneling theory (Chapter 4). The regeneration reaction is dependent on the iodide

concentration, electrolyte viscosity and dye structure. For the N719 sensitiser dye, and employing a low-viscosity electrolyte such as acetonitrile, the regeneration reaction has a half-time of $\sim 1 \mu\text{s}$, sufficiently fast to compete effectively with the competing recombination reaction and ensuring that the regeneration reaction can be achieved with unity quantum efficiency (Green *et al.*, 2005).

Efficient charge collection by the external circuit requires the time constant for electron transport within the TiO_2 matrix to be faster than charge recombination of injected electrons with the redox couple. Electron transport is a diffusive process, strongly influenced by electron trapping in localised sub-bandgap states, resulting in the dynamics being strongly dependent on position of the TiO_2 electron Fermi level: raising the Fermi level towards the conduction-band edge resulting in increased trap filling. Typical electron-transport times under solar irradiation are of the order of milliseconds (Peter and Wijayantha, 2000; Frank *et al.*, 2004). If a low-viscosity solvent such as acetonitrile is used, transport of the oxidised redox couple to the counter electrode is not rate-limiting. However, the use of higher viscosity solvents more suitable for practical device applications (for reasons of device stability) can result in significantly lower ionic diffusion constants, with the resultant iodide/triiodide concentration gradients causing significant free energy (series resistance) losses, and also potentially accelerating interfacial charge recombination.

Given the relatively slow timescale for charge transport in DSSCs compared with most other photovoltaic devices, and the extensive interfacial area available for charge recombination in the device (due to its mesoscopic structure), it is remarkable that the quantum efficiency of charge collection can approach unity. The key factor enabling this high efficiency is the slow rate constant for the interfacial charge recombination of injected electrons with the oxidised redox couple. This reaction is a multi-electron reaction, most simply being described by the equation



which must therefore proceed via one or more intermediates states. The mechanism of this reaction has been extensively studied, and while the details remain somewhat controversial, it is apparent that without a suitable catalyst such as platinum, one or more of these intermediates steps exhibits a significant activation barrier, resulting in a slow overall rate constant for this reaction. The low rate constant for this recombination reaction on TiO_2 , contrasting to the facile electrochemistry of this redox couple on the platinised counter electrode, is a key factor behind the remarkable efficiencies achieved to date for DSSCs. Nevertheless, eq. 8.1 is the primary recombination pathway in DSSCs. The flux of this recombination pathway increases with

increasing electron density in the TiO_2 electrode (and therefore with the TiO_2 Fermi level or cell voltage). In the dark it is responsible for the diode-like leakage current observed in current–voltage scans, while under illumination it is the primary factor limiting the voltage output of the device.

The kinetic competition between charge transport and recombination in DSSCs has been analysed in terms of an effective carrier diffusion length L_n , given by

$$L_n = \sqrt{D_{\text{eff}} \tau} \quad (8.2)$$

where D_{eff} is the effective electron diffusion length, and τ the electron lifetime due to the charge-recombination reaction given by eq. 8.1 (Peter and Wijayantha, 2000). D_{eff} increases with light intensity (due to the increased electron density in the TiO_2 film) whilst τ shows a proportional decrease, resulting in L_n being largely independent of light intensity. Typical values for L_n are 5–20 μm , and even 100 μm near the optimum power point for cells with >10% conversion efficiency, consistent with the high carrier-collection efficiencies observed in efficient DSSCs.

It is important to emphasize that the energetics and kinetics of DSSC function are not independent considerations. The kinetics of the interfacial electron-transfer dynamics depend strongly on the energetics of the TiO_2 /dye/electrolyte interface and on the density of electrons in the TiO_2 (*i.e.* the TiO_2 Fermi level). Raising the energy of the TiO_2 conduction band reduces recombination losses (as for a given TiO_2 Fermi level, the electron density in the TiO_2 film will be lower), and therefore may give a high cell output voltage, but at the expense of a lower free energy driving force for charge separation, which may result in a lower quantum efficiency for charge generation and therefore a lower output current. In practice, modulation of these energetics and kinetics to achieve optimum device performance remains one of the key challenges in DSSC research and development.

8.4 DSSC research and development

8.4.1 Panchromatic sensitisers

The ideal sensitiser for a single-junction photovoltaic cell converting standard global AM1.5 sunlight to electricity should absorb all light below a threshold wavelength of about 920 nm. In addition, it must also carry attachment groups such as carboxylate or phosphonate to firmly graft it to the semiconductor oxide surface. On excitation, it should inject electrons into the solid with a quantum yield of unity. The energy level

of the excited state should be well matched to the lower bound of the conduction band of the oxide to minimise energetic losses during the electron-transfer reaction. Its redox potential should be sufficiently high that it can be regenerated via electron donation from the redox electrolyte or the hole conductor. Finally, it should be stable enough to sustain about 100 million turnover cycles, corresponding to about twenty years of exposure to natural light. A single-junction device with such a sensitiser could reach a maximum conversion efficiency of 32% in global AM 1.5 sunlight.

Much of the research in DSSC dye chemistry is devoted to the identification and synthesis of sensitisers matching these requirements, while retaining stability in the photoelectrochemical environment. The attachment group of the dye ensures that it spontaneously assembles as a molecular layer on exposing the oxide film to a dye solution. This molecular dispersion ensures a high probability that, once a photon is absorbed, the excited state of the dye molecule will relax by electron injection into the semiconductor conduction band. However, the optical absorption of a single monolayer of dye is weak, a fact which originally was cited as ruling out the possibility of high-efficiency sensitised devices, as it was assumed that smooth substrate surfaces would be imperative in order to avoid the recombination loss mechanism associated with rough or polycrystalline structures in solid-state photovoltaics. This objection was invalidated by recognising that the injection process places electrons in the semiconductor lattice, spatially separated from the positive charge carriers by the dye molecules, which are insulating in the ground state and hence provide a barrier for charge recombination. By now, the use of nanocrystalline thin-film structures with a roughness factor of >1000 has become standard practice.

The best photovoltaic performance in terms of both conversion yield and long-term stability has so far been achieved with polypyridyl complexes of ruthenium and osmium. Sensitisers having the general structure $ML_2(X)_2$ where L stands for 2,2'-bipyridyl-4,4'-dicarboxylic acid, M is Ru or Os, and X represents a halide, cyanide, thiocyanate, acetyl acetonate, thiocarbamate or water substituent, are particularly promising. Thus, the ruthenium complex *cis*- $RuL_2(NCS)_2$, known as N3 dye, has become the paradigm heterogeneous charge-transfer sensitiser for mesoporous solar cells (Nazeeruddin *et al.*, 1993). The absorption spectrum of fully protonated N3 has maxima at 518 and 380 nm, with extinction coefficients of $1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $1.33 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The complex emits at 750 nm, the excited-state lifetime being 60 ns. The optical transition has MLCT (metal-to-ligand charge-transfer) character: excitation of the dye involves transfer of an electron from the metal to the π^* orbital of the surface-anchoring carboxylated bipyridyl ligand, from where it is released in a timescale of femtoseconds to picoseconds into the conduction band of TiO_2 , generating electric charges with unit quantum yield.

Discovered in 1993, the photovoltaic performance of N3 has been unmatched for eight years by virtually hundreds of other complexes that have been synthesised and tested. However, in 2001 the ‘black dye’ tri(cyanato)-2,2'2''-terpyridyl-4,4'4''-tricarboxylate)Ru(II) achieved 10.4% AM1.5 solar-to-power conversion efficiency in full sunlight (Nazeeruddin *et al.*, 2001). Conversion efficiencies have meanwhile been improved further, the current record validated by an accredited laboratory being 11.1% (Chiba *et al.*, 2006).

Figure 8.6 compares the spectral response of the photocurrent observed with the N3 dye and the black dye sensitisers. The incident photon-to-current conversion efficiency (IPCE) of the DSSC is plotted as a function of excitation wavelength. Both chromophores show very high IPCE values in the visible range. However, the response of the black dye extends 100 nm further into the IR than that of N3. The photocurrent onset is close to 920 nm, near the optimal threshold for single-junction converters. From there the IPCE rises gradually until at 700 nm it reaches a plateau of ~80%. If one accounts for reflection and absorption losses in the conducting glass, the conversion of incident photons to electric current is practically quantitative over the whole visible domain. From the overlap integral of the black dye curves in Fig. 8.6 with the AM 1.5 solar spectrum, the short-circuit photocurrents of the N3 and black dye-sensitised cells are predicted to be 16 mA cm^{-2} and 20.5 mA cm^{-2} respectively, in agreement with experimental observations. Employing antireflective coatings and optimising light-scatter effects to capture more photons in the near-IR regions can increase the photocurrents to a maximum of 18 mA cm^{-2} and 22 mA cm^{-2} for the two

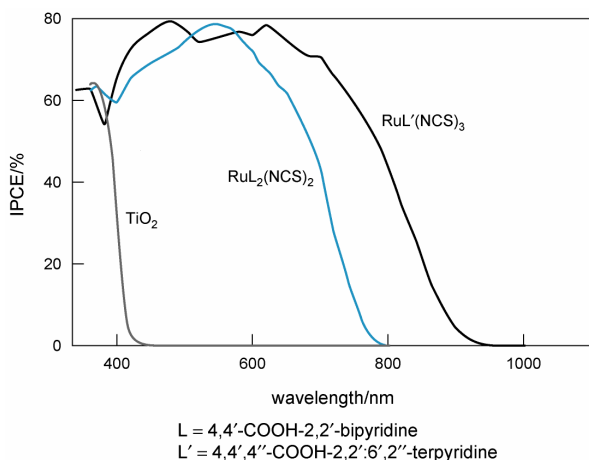


Figure 8.6 Spectral response of the photocurrent for mesoscopic injection solar cells. Grey curve: bare TiO_2 film, blue and black curves: same film sensitised by the N3 and black ruthenium dyes, respectively.

dyes under standard reporting conditions (SRC). Any higher values point to a spectral mismatch between the output of the simulator and AM1.5 sunlight. The overall maximum-power efficiency (η_{mp}) of the cell is calculated from the integral short-circuit photocurrent density (i_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (η_{fill}) and the incident solar irradiance ($E_s^0 = 1000 \text{ W m}^{-2}$) as

$$\eta_{\text{mp}} = i_{\text{sc}} \times V_{\text{oc}} \times \eta_{\text{fill}} / E_s^0 \quad (8.3)$$

8.4.2 Opportunities for performance improvement

The solar-to-electric power conversion efficiency of DSSC laboratory cells, validated by an accredited PV calibration laboratory, has reached 11.1% under standard reporting conditions, *i.e.* air mass 1.5 global sunlight at 1000 W m^{-2} intensity and 298 K temperature (Chiba *et al.*, 2006), rendering the DSSC a credible alternative to conventional *p-n* junction photovoltaic devices. Figure 8.7 shows the photovoltaic performance data of such a champion cell. A couple of years ago, solid-state equivalents using organic hole conductors reached an efficiency of 4.2% (Schmidt-Mende *et al.*, 2005b), and recently Snaith *et al.* (2007) have reported an efficiency of 5.1%, whereas nanocomposite films comprising only inorganic materials, such as TiO_2 and CuInS_2 , have achieved efficiencies between 5% and 6% in the ETA cells discussed by Könenkamp in Chapter 6 (see also Fig. 1.2 and Nanu *et al.*, 2005).

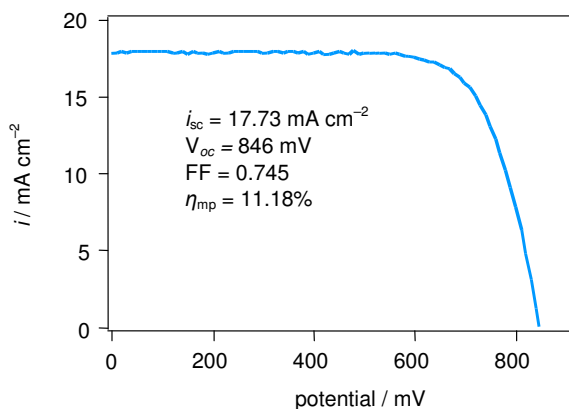


Figure 8.7 Photovoltaic performance of a state-of-the-art DSSC laboratory cell: i - V curve measured under AM 1.5 standard test conditions.

Judicious molecular engineering of the ruthenium dye structure will allow further increase of light harvesting in the 700–900 nm region. Ruthenium complexes of quaterpyridyl derivatives show great promise in this respect. The goal is to obtain a DSSC having optical features similar to those of GaAs. A nearly vertical rise of the photocurrent close to the 920 nm absorption threshold would increase the short-circuit photocurrent from currently 20.5 mA cm⁻² to about 28 mA cm⁻², raising the overall efficiency to over the 15% mark without changing the currently used redox system. Ultimately the combination of two sensitizers, one being the red or black ruthenium complex and the other an organic dye showing strong absorption in the near-infrared region, may be required to achieve this desired spectral response. Such dye ‘cocktails’ are presently under intense investigation and the first results look promising (Reddy *et al.*, 2007). A road map to achieve this goal by the year 2009 has been elaborated and will serve to coordinate synthetic efforts of several groups on the international scale.

8.4.3 Tandem cells

A feature that makes the DSSC particularly attractive for tandem cell application is that its optical transmission and short-circuit photocurrent can be readily adjusted by changing the film thickness, pore size, the nature of the dye and the dye loading. This, along with the ease of forming layered structures, for example by producing the

mesoscopic oxide films using screen printing or doctor blading methods, renders the DSSC particularly well suited for the fabrication of tandem solar cell structures that capture the solar emission in an optimal fashion. Note that for a two-level tandem cell a conversion efficiency of up to 47% can be reached, the optimal bandgaps for the top and bottom cells being around 1.65 eV and 1 eV respectively.

Several publications have dealt with the use of stacked DSSC configurations in which two dyes absorbing different parts of the solar spectrum serve as sensitisers (Durr *et al.*, 2004; Kubo *et al.*, 2004). We recently demonstrated that a tandem device comprising a DSSC as a top cell for high-energy photons and a copper indium gallium selenide (CIGS) thin-film bottom cell, capturing the red and near-IR solar emission respectively, produces AM1.5 solar-to-electric conversion efficiencies greater than 15% (Liska *et al.*, 2006).

Figure 8.9 shows the i - V curve and other characteristics obtained under AM 1.5 insolation for one of the first embodiments of this two-terminal tandem device. The performance of the tandem was clearly superior to that of the individual cells, despite the fact that the short-circuit currents of the two cells were not perfectly matched, as evidenced by the shoulder in the i - V curve. Likewise, no effort was made to minimise the optical losses. This leaves no doubt that further rapid efficiency gains reaching well beyond the 20% mark can be expected from the fructuous marriage of these two thin-film PV technologies (Liska *et al.*, 2006). Combining a relatively low-cost thin-film CIGS substrate cell with a DSSC superstrate cell may be a cheaper method of achieving efficiencies above 15% than use of a high-efficiency CIGS cell alone.

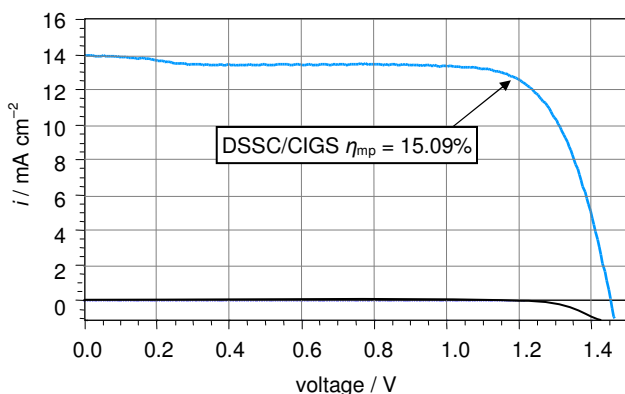


Figure 8.9 Photocurrent density–voltage characteristics under AM 1.5 full sunlight (1000 mW cm^{-2}) for a two-terminal tandem DSSC/CIGS cell. The DSSC top cell produced $i_{\text{sc}} = 13.66 \text{ mA cm}^{-2}$; $V_{\text{oc}} = 0.8 \text{ V}$; FF = 0.75 and $\eta = 8.2\%$, while the CIGS bottom cell produced $i_{\text{sc}} = 14.3 \text{ mA cm}^{-2}$; $V_{\text{oc}} = 0.65 \text{ V}$ and FF = 0.77 and $\eta = 7.28\%$. The DSSC/CIGS tandem cell produced $i_{\text{sc}} = 14.05 \text{ mA cm}^{-2}$; $V_{\text{oc}} = 1.45 \text{ V}$; FF = 0.74 and $\eta = 15.09\%$. The reverse-bias characteristics are shown as a black curve. Adapted from Liska *et al.* (2006).

8.4.4 Stability

Unlike amorphous silicon, which suffers from degradation due to the well-known Staebler–Wronski effect, the intrinsic stability of the DSSC has been confirmed by extensive accelerated light-soaking tests carried out over the last decade. One major issue that has been settled during this period is that the sensitisers employed in the current DSSC embodiments can sustain twenty years of outdoor service without significant degradation. However, as new and more advanced dye structures emerge, and in order to avoid repeating these lengthy tests every time the sensitiser is modified, kinetic criteria have been developed to allow prediction of long-term sensitiser performance.

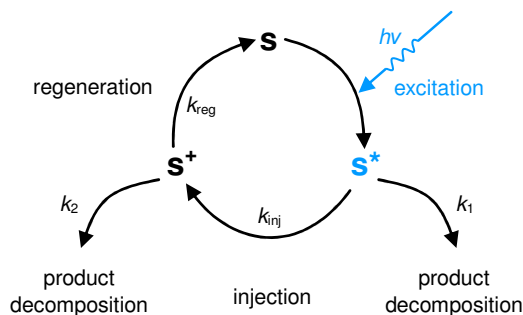


Figure 8.10 The catalytic cycle of the sensitiser during DSSC operation.

Figure 8.10 illustrates the catalytic cycle that the sensitiser undergoes during cell operation. Critical for stability are side reactions that occur from the excited state (S^*) or the oxidised state of the dye (S^+), which would compete with electron injection from the excited dye into the conduction band of the mesoscopic oxide and with the regeneration of the sensitiser. These destructive channels are assumed to follow first or pseudo-first order kinetics and are assigned the rate constants k_1 and k_2 . Introducing the two branching ratios $P_1 = k_{inj}/(k_1 + k_{inj})$ and $P_2 = k_{reg}/(k_2 + k_{reg})$, where k_{inj} and k_{reg} are the first order or pseudo-first order rate constants for the injection and regeneration process, respectively, the fraction of the sensitiser molecules that survives one cycle is given by the product $P_1 \times P_2$. A simple calculation (Grätzel, 2006) shows that the sum of the branching ratios for the two bleeding channels should not exceed 1×10^{-8} in order for the lifetime of the sensitiser to reach at least twenty years. The turnover frequency of the dye in the working DSSC, averaged diurnally and seasonally, is about 0.16 s^{-1} .

For most of the common sensitisers, the rate constant for electron injection from the excited state of the dye to the conduction band of the TiO_2 particles is in the femtosecond range. Assuming $k_{\text{inj}} = 10^{11} - 10^{13} \text{ s}^{-1}$, any destructive side reaction should have $k_1 < 10^2 \text{ s}^{-1}$. Ruthenium sensitisers of the N719 or K-19 type readily satisfy this condition as the decomposition from the excited-state level occurs at a much lower rate than the 10^2 s^{-1} limit. Precise kinetic information has also been gathered for the second destructive channel involving the oxidised state of the sensitiser, the key parameter being the ratio k_2/k_{reg} of the rate constants for the degradation of the oxidised form of the sensitiser and its regeneration. The S^+ state of the sensitiser can readily be produced by chemical or electrochemical oxidation and its lifetime can be independently determined by absorption spectroscopy. A typical value of k_2 is around 10^{-4} s^{-1} while the regeneration rate constant is at least in the 10^5 s^{-1} range. Hence the branching ratio is well below the limit of 10^{-8} , which can be tolerated to achieve the 100 million turnovers and a 20-year lifetime for the sensitiser.

Many long-term tests which have been performed with the N3-type ruthenium complexes have confirmed the extraordinary stability of these charge-transfer sensitisers. For example, a European consortium supported by the Joule program (Hinsch *et al.*, 2001) confirmed cell photocurrent stability during 8,500 hours of light soaking at 2.5 Suns, corresponding to about 56 million turnovers of the dye without any significant degradation. These results corroborate the projections from the kinetic considerations made above. A more difficult task has been to achieve stability under prolonged stress at higher temperatures, *i.e.* 80–85 °C. The introduction of hydrophobic sensitisers has been particularly rewarding in allowing the DSSC to meet, for the first time, the specifications laid out for outdoor applications of silicon photovoltaic cells (Wang *et al.*, 2003a). In addition these dyes show enhanced extinction coefficients due to the extension of the π conjugation onto one of the bipy ligands by styrene moieties. Taking advantage of these properties and using a novel robust electrolyte formulation, a $\geq 8\%$ efficient DSSC has been realised that shows strikingly stable performance under both prolonged thermal stress and light soaking (Wang *et al.*, 2005b).

While impressive progress has been made in the development of stable, non-volatile electrolyte formulations, the conversion yields obtained with these systems are presently in the 7–10% range, below the 11.1% reached with volatile solvents. Future research efforts will be dedicated to bridging the performance gap between these systems. The focus will be on hole conductors and solvent-free electrolytes such as ionic liquids. The latter are a particularly attractive choice for the first commercial modules, owing to their high stability, negligible vapour pressure and excellent compatibility with the environment.

8.4.5 Organic dyes

When considering organic dyes for use in DSSCs, porphyrins and phthalocyanines have attracted particular attention, the former because of the analogy with natural photosynthetic processes, the latter because of their photochemical and phototherapeutic applications. However, porphyrins cannot compete with the N3 or black dye sensitizer due to their lack of red light and near-IR absorption. Phthalocyanines, on the other hand, show intense absorption bands in this spectral region. However, problems with aggregation and the unsuitable energetic position of the LUMO level, which is too low for electron transfer to the TiO_2 conduction band, have turned out to be intractable for the moment.

More recently, the groups of Arakawa and Uchida have made remarkable advances in the development of organic dyes for use in DSSCs (Horiuchi *et al.*, 2004; Hara *et al.*, 2005). Using coumarin or polyene-type sensitizers, strikingly high solar-to-electric power conversion efficiencies, reaching up to 9.2% in full sunlight (Ito *et al.*, 2006), have been achieved in liquid-electrolyte cells. The rational design of such sensitizers based on quantum mechanical considerations has made great progress during the last few years, and replacement of ruthenium sensitizers by such molecularly engineered dyes is likely to occur in the near future.

8.4.6 Quantum dots as sensitizers

Semiconductor quantum dots are another attractive option for panchromatic sensitizers. These are II–VI and III–V type semiconductor particles whose size is small enough to produce quantum confinement effects of the type discussed by Nozik in Chapter 3. The absorption spectrum of such quantum dots can be adjusted by changing the particle size. Thus, the bandgap of materials such as InAs and PbS can be adapted to attain the value of 1.35 eV, which is ideal for a single-junction solar quantum converter. During the last decade a wealth of information has been gathered on the physical properties of quantum-dot materials and research is being pursued very actively. One problem with this approach is the photocorrosion of the quantum dots that will almost certainly happen if the junction contact is a liquid redox electrolyte. However quantum dots are expected to display higher stability in solid-state heterojunction devices (Plass *et al.*, 2002). The advantage of Q-dots over conventional dyes as sensitizers is their very high extinction coefficients, which allows thinner films of the mesoporous oxide to be used. This should reduce the dark current, increasing V_{oc} and the overall efficiency of the cell.

An exciting discovery made in recent years is that multiple exciton generation (MEG) can be obtained from the absorption of a single photon by a quantum dot if the photon energy is at least two times higher than its bandgap (Nozik, 2003; Schaller and Klimov, 2004). The challenge is now to find ways to collect the excitons before they recombine. As recombination occurs on a picosecond time scale, the use of mesoporous oxides as electron collectors presents a promising strategy, because the electron transfer from the quantum dot to the conduction band of the oxide electrode occurs within femtoseconds (Plass *et al.*, 2002). As Nozik points out in Chapter 3, this opens up research avenues that ultimately may lead to photon converters reaching external quantum efficiencies values of several hundred percent. A calculation based on Henry's model (Henry, 1980) shows that the maximum conversion efficiency of a single-junction cell could be increased from 34% to 44% by exploiting MEG effects.

8.4.7 Mesoporous oxide film development

When the dye-sensitised nanocrystalline solar cell was first presented, perhaps the most puzzling phenomenon was the highly efficient charge transport through the nanocrystalline TiO₂ layer. Mesoporous electrodes differ greatly from their compact analogs because (i) the inherent conductivity of the film is very low; (ii) the small size of the nanocrystalline particles does not support a built-in electrical field; and (iii) the electrolyte penetrates the porous film all the way to the back contact, making the semiconductor/electrolyte interface essentially three-dimensional. The mechanism of charge transport in mesoporous systems is under keen debate today and several interpretations based on the Montrol–Scher model for random displacement of charge carriers in disordered solids have been advanced (Nelson and Chandler, 2004). However, the 'effective' electron diffusion coefficient is expected to depend on a number of factors such as trap filling and space-charge compensation by ionic motion in the electrolyte. The theoretical and experimental effort will continue as there is a need for further in-depth analysis of this intriguing charge-percolation process. The factors controlling the rate of charge-carrier percolation across the nanocrystalline film are presently under intense scrutiny. Intensity-modulated impedance spectroscopy (see Section 12.6) has proved to be an elegant and powerful tool (Bisquert, 2002; Kubo *et al.*, 2002; Cass *et al.*, 2003; Frank *et al.*, 2004; Cass *et al.*, 2005; Fabregat-Santiago *et al.*, 2005) to address these and other important questions related to the characteristic time constants for charge-carrier transport and reaction dynamics in dye-sensitised nanocrystalline solar cells.

On the material science side, future research will be directed towards synthesising structures with a higher degree of order than a random assembly of nanoparticles. A desirable morphology of the films would have the mesoporous channels or nanorods aligned in parallel to each other and vertically with respect to the TCO glass current collector. This would facilitate pore diffusion, give easier access to the film surface, avoid grain boundaries and allow the junction to be formed under better control. One approach to fabricate such oxide structures is based on surfactant template-assisted preparation of TiO_2 nanotubes, as described by Jiu *et al.* (2005). These and the hybrid nanorod–polymer composite cells developed by Alivisatos and co-workers (Huynh *et al.*, 2002) have confirmed the superior photovoltaic performance of such films as compared with random-particle networks.

8.4.8 Molecular engineering of the interface

The high contact area of the junction in nanocrystalline solar cells renders mandatory the grasp and control of interfacial effects for future improvement of cell performance. The nature of the exposed surface planes of the oxide and the mode of interaction with the dye is the first important information to gather. As far as the adsorption of the N3 dye on TiO_2 is concerned, this is now well understood. The prevalent orientation of the anatase surface planes is (101) and the sensitiser is adsorbed through two of the four carboxylate groups, at least one of them being anchored via a bidentate configuration bridging two adjacent titanium sites (Nazeeruddin *et al.*, 2000). Molecular dynamic calculations employing a classical force field have been carried out to predict the equilibrium geometry of the adsorbed sensitiser state (Burnside *et al.*, 1998; Shklover *et al.*, 1998). More sophisticated first-principle density functional calculations have also been undertaken (Vittadini *et al.*, 1998) to model the surface interactions of TiO_2 with simple adsorbates as well as the surface reconstruction effects resulting from the adsorption. The latter approach is particularly promising and will provide an important tool for future theoretical investigations.

Synthetic efforts focus on the molecular engineering of sensitisers that enhance charge separation at the oxide solution interface. The structural features of the dye should match the requirements for current rectification: by analogy to the photofield effect in transistors, the gate for unidirectional electron flow from the electrolyte through the junction and into the oxide is opened by the photoexcitation of the sensitiser. The reverse charge flow, *i.e.* recapture of the electron by the electrolyte, could be impaired by judicious design of the sensitiser. The latter should form a

tightly packed insulating monolayer blocking the dark current. The gain in open-circuit voltage can be calculated from the diode equation

$$V_{oc} = (nRT/F) \ln[(i_{sc}/i_o) - 1] \quad (8.4)$$

where n is the ideality factor, whose value is between 1 and 2 for DSSCs, and i_o is the reverse saturation current. Thus for each order of magnitude decrease in the dark current, the gain in V_{oc} would be 59 mV at room temperature. Work in this direction is indispensable to raise the efficiency of the DSSC significantly over the 15% limit with the currently employed redox electrolytes.

8.5 Solid-state dye-sensitised cells

Research on solid-state DSSCs has gained considerable momentum in recent years as this embodiment is attractive for realising flexible PV cells in a roll-to-roll production (www.konarka.com). The most successful p -type organic conductor employed to date is *spiro*-OMeTAD, which has a work function of ~ 4.9 eV and hole mobility of $2 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ (see Fig. 8.11). First reported in 1998, conversion efficiencies of solid-state cells incorporating this hole conductor have increased dramatically over the last few years, from a fraction of a percent (Bach *et al.*, 1998) to over 4% (Schmidt-Mende *et al.*, 2005a). The main drawback of these cells has been fast interfacial electron-hole recombination, reducing the electron diffusion length to a few microns (Kruger *et al.*, 2003) as compared with 20–100 μm for electrolyte-based DSSCs. This restricts the film thickness employed in these cells to only 2 μm , which is insufficient for the adsorbed sensitiser to harvest all incident sunlight, thus reducing the photocurrent. The dye monolayer can block this back reaction to some extent because it is electrically insulating (Snaith *et al.*, 2005). Hence current efforts are directed towards molecular engineering of the interface to improve the compactness and order of the monolayer and prevent charge carriers from recombining.

Another difficulty that has been encountered has been the filling of the porous network with the hole conductor. This impediment may be overcome by developing oxide films having regular mesoporous channels aligned perpendicular to the current collector. On the other hand, the V_{oc} values obtained with solid-state DSSCs are high, reaching nearly 1 V, owing to a better match of the hole conductor work function than that of the electrolyte with the redox potential of the sensitiser. The future of these solid hole-conductor systems thus looks very bright if the recombination and pore filling problems can be solved.

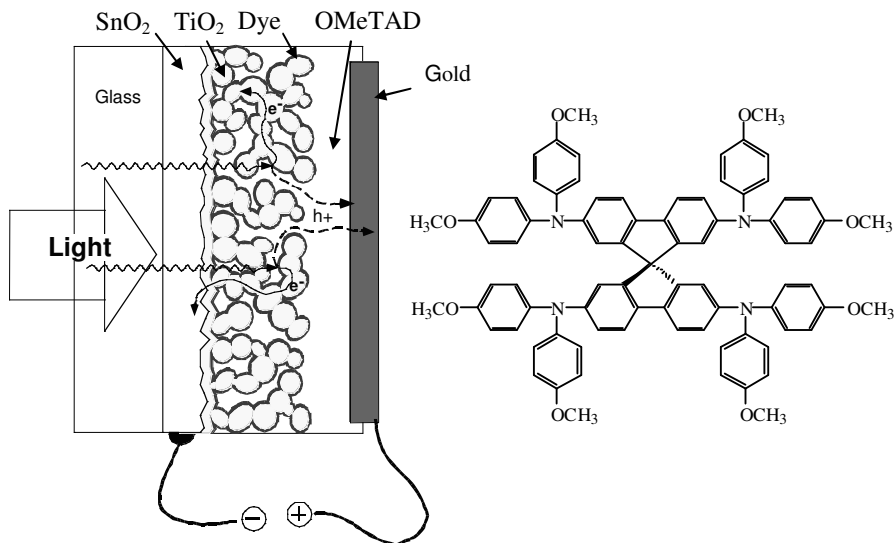


Figure 8.11 Cross-sectional view of a solid-state DSSC containing the hole conductor *spiro*-OMeTAD, the structure of which is indicated on the right (left drawing courtesy B. O'Regan).

8.6 Pilot production of modules, outdoor field tests and commercial DSSC development

Figure 8.12 shows two prototypes of the monolithic Z-type interconnected DSSC modules, fabricated by Aisin Seiki in Japan, using carbon as a back contact to cut costs. Comparative field tests of these modules and polycrystalline silicon (pc-Si) have been running for several years; Figure 8.13 shows a photograph of the test station. The test results revealed the advantages of the DSSC as compared with silicon modules under realistic outdoor conditions: for equal rating under standard test conditions (STC), the DSSC modules produced 20–30% more energy than pc-Si modules (Toyoda, 2006). The superior performance of the DSSC can be ascribed to the following factors:

- The DSSC efficiency is practically temperature-independent in the range 25–65 °C while that of monocrystalline and pc-Si declines by ~20% over the same range.
- Outdoor measurements indicate that light capture by the DSSC is less sensitive to the angle of incidence, although this needs to be further assessed.
- The DSSC is more efficient than pc-Si in diffuse light or cloudy conditions.

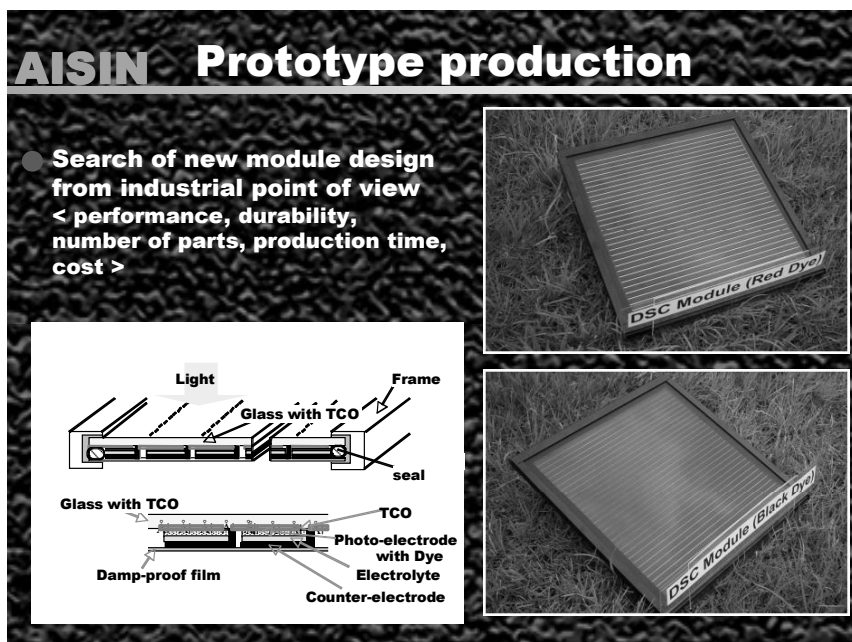


Figure 8.12 Production of DSSC prototypes by Aisin Seiki in Japan. Note the monolithic design of the PV modules and the use of carbon as interconnect and counter electrode. The red dye is related to N-719 while the black dye has the structure $\text{RuL}'(\text{NCS})_3$ where $\text{L}' = 2, 2', 2''$ -terpyridyl, 4,4',4''-tricarboxylic acid. The hole conductor is a non-volatile electrolyte.

While it is up to the commercial supplier to set the final price for such modules, it is clear that the DSSC shares the cost advantages of all thin-film devices. In addition it uses no high-vacuum, cost-intensive steps and only cheap and readily available materials. Although it might be thought that the ruthenium-based sensitizer adds high material cost, its contribution to cost is $< \text{€ } 0.01 \text{ W}_p^{-1}$ because of the small amount used. Also purely organic sensitizers can now achieve practically the same efficiency as Ru complexes. Given these advantages at comparable conversion efficiency, module costs below $\text{€ } 1 \text{ W}_p^{-1}$ are realistic targets even for production plants having well below GW capacity. The DSSC has thus become a viable contender for large-scale solar energy conversion systems on the basis of cost, efficiency, stability and availability, as well as environmental compatibility. Building-integrated DSSC panels have been installed in the walls of the Toyota 'Dream House' shown in Fig. 8.14, and the British company G24i (www.G24i.com) has recently announced the building of the first 20 MW DSSC manufacturing plant in Wales.

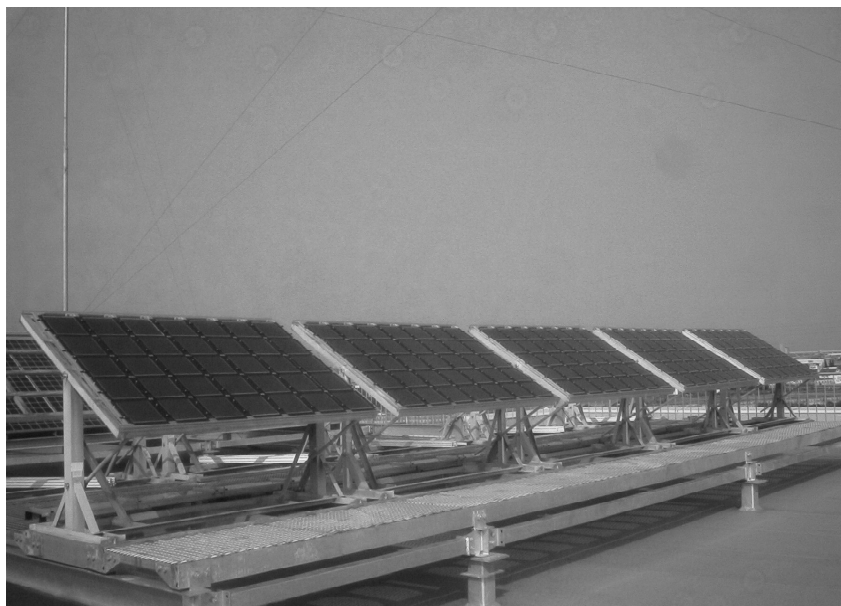


Figure 8.13 Outdoor field tests of DSSC modules in Kariya City, Japan at latitude $35^{\circ}10'N$. Azimuthal angle 0° , facing due south, tilt angle 30° . Note the pc-Si modules in the second row.



Figure 8.14 The Toyota 'Dream House' featuring DSSC panels made by Aisin Seiki (http://www.toyota.co.jp/jp/news/04/Dec/nt04_1204.html)

8.7 Outlook

Using a principle derived from natural photosynthesis, mesoscopic injection solar cells, and in particular the DSSC, have become a credible alternative to solid-state *p-n* junction devices. Conversion efficiencies over 11% and 15% have already been obtained with single-junction and tandem liquid-electrolyte cells, respectively, on the laboratory scale, but there is ample room for further amelioration. Future research will focus on improving the short-circuit current by extending the light response of the sensitisers in the near-IR spectral region. Substantial gains in the open-circuit voltage are expected from introducing ordered oxide mesostructures and controlling the interfacial charge recombination by judicious engineering on the molecular level. Hybrid cells based on solid-state inorganic and organic hole conductors are an attractive option, in particular for the flexible DSSC embodiment. Nanostructured ETA cells using purely inorganic components, discussed by Könenkamp in Chapter 6, will also be developed.

Mesoscopic dye-sensitised cells are well suited for a whole realm of applications, ranging from the low-power market to large-scale applications. Their excellent performance in diffuse light gives them a competitive edge over silicon in providing electric power for stand-alone electronic equipment both indoors and outdoors. DSSCs are already being applied in building-integrated PV and this will become a fertile field of future commercial development.

As the quotation at our chapter head shows, at the 1912 IUPAC conference in Washington almost one hundred years ago the famous Italian photochemist Professor Giacomo Ciamician predicted that mankind will unravel the secrets of photosynthesis and apply the principles used by plants to harvest solar energy in glass buildings. His visionary thoughts appear now close to becoming a reality.

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SEMICONDUCTOR/LIQUID JUNCTION PHOTOELECTROCHEMICAL SOLAR CELLS

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*More energy from the Sun hits the Earth in one hour than all
of the energy consumed on the planet in an entire year.*

9.1 Introduction

Efficient and sustained conversion of sunlight into electrical and/or chemical energy by a photoelectrochemical system requires several processes. A substantial fraction of the incident solar radiation must be absorbed and must generate spatially separate excited electrons and electron-vacancies (holes). The photogenerated charge carriers need to be rapidly directed to sites that favour charge transfer to species in solution over processes that produce wasteful charge-carrier recombination. The desired photoelectrochemical reaction(s) must have the proper thermodynamic driving force, possess sufficiently rapid reaction kinetics, and be free of competing or deleterious chemical side reactions. In total, the operational efficiency of a photoelectrochemical system depends strongly on the materials properties of each component, and critically on the associated interfacial physicochemical and electrochemical properties.

Crystalline inorganic semiconductors are well suited for absorption of sunlight and effective electron–hole separation. Inorganic semiconductor absorbance coefficients for photons with greater than bandgap energies are $\sim 10^2\text{--}10^5\text{ cm}^{-1}$, and charge-carrier mobilities within crystalline inorganic semiconductors are $\sim 10^2\text{--}10^3\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ (Sze 1981; Stanton *et al.*, 2003). Since the bandgap energy determines the threshold for light absorption in an inorganic semiconductor, materials with small bandgaps that match the energies of solar photons with the highest flux (*i.e.* near-infrared and visible light) are natural candidates for efficient photoelectrodes (Fig. 9.1). As early as the 1950s, researchers at Bell Laboratories explored the use of small-bandgap semiconductors in modern photoelectrochemical cells (Law and Meigs, 1955). However, these workers quickly determined that the available small-bandgap semiconductors

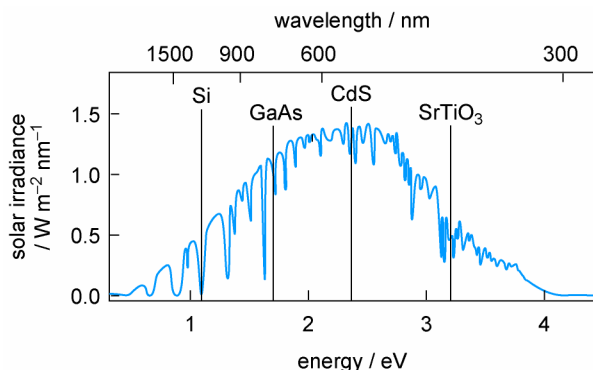


Figure 9.1 Solar irradiance at the surface of the Earth. The dark lines denote the bandgap energies of Si, GaAs, CdS and SrTiO_3 , respectively at $T = 300$ K. The portions of the spectrum to the left of each line represent photons that are not substantially absorbed by the semiconductor.

were much too susceptible to corrosion and/or oxidation in water to be readily useful in aqueous photoelectrochemical systems. This observation tempered further exploration of photoelectrochemical cells for nearly twenty years, until researchers at Kanagawa University in Japan discovered that a metal oxide semiconductor photoelectrode could support sustained water electrolysis (Fujishima and Honda, 1972; Wrighton *et al.*, 1975; Kung *et al.*, 1977). Soon thereafter, fervent efforts by several research groups led to the discovery and development of several other stable metal oxide materials for continuous light-driven fuel formation of H_2 and O_2 from water (Mavroides *et al.*, 1976; Alkaiatis and Rauh, 1979; Koffyberg, 1979; Rauh *et al.*, 1979; Amarakoon and Payne, 1980; Morisaki *et al.*, 1980; Giordano *et al.*, 1983; Leygraf *et al.*, 1983). Frustratingly, these active metal oxide semiconductors possess bandgap energies that are too large to absorb appreciable amounts of sunlight. Consequently, photoelectrochemical cells using these materials are limited to very low overall energy conversion efficiencies of $\leq 1\%$, as shown in Fig. 9.1 and Table 9.1 (at the end of this chapter).

Activity in the field of photoelectrochemistry has since been directed towards bridging the ‘gap’ between systems that can absorb sunlight effectively and those that can support prolonged operation with reasonable energy-conversion efficiencies. There is no inherent, fundamental tenet or natural law that precludes a semiconductor from both being a good absorber of sunlight and being physically, chemically and electrically stable during cell operation. Rather, experimental evidence demonstrates that rational design of photoelectrochemical systems can overcome many initially perceived obstacles. In this chapter, we provide a general overview of the cumulative

progress made towards understanding and optimising the photoelectrochemical behaviour of the semiconductor/solution interface, as summarised in Table 9.1. Although not exhaustive, the experimental results presented and discussed herein highlight some of the advances in the development of solar energy conversion devices based on light-harvesting photoelectrochemical cells. These advances can be separated into five distinct categories: (a) manipulation of the interfacial junction energetics and stability via the choice of the solution redox couple; (b) use of non-corrosive (non-aqueous) solvents; (c) chemical modification and passivation of the semiconductor surface; (d) sensitisation of the semiconductor surface with a light-absorbing dye; and (e) creation of multi-junction architectures through the use of two or more semiconductors. The first three approaches are the foci of this chapter, while the latter two are discussed in detail in Chapters 8 and 10, respectively.

9.2 Variation of the solution redox couple

The energetics and stability of a semiconductor/liquid interface are strongly influenced by the electrochemical properties of the redox couple dissolved in the solution. In this section, the basic principles involved in charge transfer at photoelectrochemical junctions are defined and discussed. In addition, experimental strategies that focus on the specific chemical nature of the dissolved redox couple for inhibiting semiconductor oxidation and corrosion are described.

9.2.1 Interfacial energetics

Thermodynamic control The bottom of the conduction band at the surface, E_c , the top of the valence band at the surface, E_v , and the Fermi level, E_F , are important energetic properties of a semiconductor (Fig. 9.2). For a solution containing both the oxidised and reduced forms of a redox couple, the nernstian potential (in units of V vs. a normal hydrogen reference electrode; Bard and Faulkner, 1980) is $U(A/A^-)$, where A and A^- are the acceptor and donor halves of the redox couple. The Fermi level of the solution containing the redox couple A/A^- is $-qU(A/A^-)$, where q is the unsigned charge of an electron. The initial difference between the semiconductor and solution Fermi levels (Fig. 9.2a) determines the size of the energy barrier at the semiconductor/liquid junction when the interface reaches equilibrium, at which point $E_F = -qU(A/A^-)$, as shown in Fig. 9.2b. Figure 9.2 shows the situation for an *n*-type semiconductor/solution interface, but a conceptually identical situation occurs for *p*-

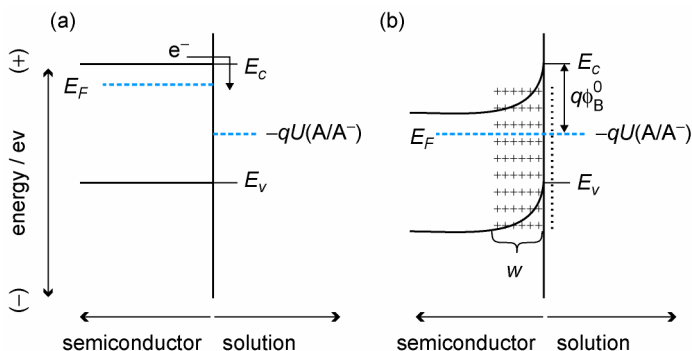


Figure 9.2 Before (a) and after (b) equilibration of the semiconductor Fermi level, E_F , with the solution nernstian potential, $U(A/A^-)$. A space-charge region with width w develops which produces a spatially dependent electric potential drop in the solid. At equilibrium in the absence of illumination, the electrode potential is such that the Fermi level of the semiconductor, E_F , equals $qU(A/A^-)$.

type semiconductor/solution interfaces. For the system to reach equilibrium, charge will pass between the semiconductor and solution until the difference in the Fermi levels of the two phases is zero. Since there is no formal density of states in the bandgap of the semiconductor, the energy value of E_F in the semiconductor changes much more than $-qU(A/A^-)$, with the near-surface region of the semiconductor becoming entirely depleted of electrons. An excess of positive charges develops over a width w ($\sim 10^{-8}$ – 10^{-6} m for non-degenerately doped semiconductors) within the semiconductor, typically referred to as the depletion region. Similarly, the solution acquires an excess of anions at the interface, but across a much smaller length scale ($\sim 10^{-9}$ m).

The thermodynamic upper limit on the energy that can be extracted from the separated, photogenerated electron–hole pairs in the semiconductor is the difference between E_c and $-qU(A/A^-)$. This energetic quantity is formally known as the equilibrium barrier height, $q\phi_b^0$, where ϕ_b^0 is in units of V.¹

$$q\phi_b^0 = E_c - E_F = E_c + qU(A/A^-) \quad (9.1)$$

For uncomplicated semiconductor/liquid junctions at zero bias, the height of the interfacial barrier varies linearly with the value of $-qU(A/A^-)$. For all semiconductor/

¹ The size of barrier height, ϕ_b , at the semiconductor/solution interface for an *n*-type semiconductor is defined by the difference between E_c and E_F at all times. When E_F is perturbed away from the open-circuit potential of the system in the dark (*i.e.* $-qU(A/A^-)$) by an applied bias or photon flux, ϕ_b will not always necessarily equal $q\phi_b^0$.

liquid junctions, the equilibrium barrier height is maximised when $-qU(A/A^-)$ is at E_v (or at E_c for p -type semiconductors), *i.e.* ϕ_b^0 equals the full bandgap energy of the semiconductor. Experimentally, ϕ_b^0 is most commonly estimated by extrapolating the 'dark' current–potential or 'dark' capacitance–potential responses of the semiconductor/liquid junction to zero bias (equilibrium) (Sze, 1981). For semiconductor/liquid junctions under illumination, a related quantity, the photovoltage at open circuit (V_{oc}), reflects the maximum free energy that can be harnessed from photogenerated charge carriers. As discussed below, while V_{oc} is strongly correlated with ϕ_b^0 , variations in illumination intensity and in the transport and recombination of charge carriers within the semiconductor also influence V_{oc} . Hence, under illumination, the useable free energy of photogenerated charge carriers collected across a semiconductor/liquid junction is not purely determined by the thermodynamic properties of the interface, but is also influenced by the steady-state illumination and charge transport conditions (Lewis, 1984).

Prior to 1980, an ideal linear dependence of the experimentally measured ϕ_b^0 with $U(A/A^-)$ was rarely, if ever, observed in photoelectrochemical systems. In fact, most of the studied systems exhibited relatively little or no sensitivity of the semiconductor/liquid junction equilibrium barrier height towards the electrochemical properties of the redox couple in solution (Tributsch *et al.*, 1979; Bard *et al.*, 1980; Bocarsly *et al.*, 1980). Correspondingly, under illumination, experimental observables such as V_{oc} were seemingly fixed at low values. At the time, these observations implied an inherent pinning of the semiconductor Fermi level for all semiconductor/liquid junctions, akin to the Fermi-level pinning observed in semiconductor/metal (Schottky) junctions, which limits $q\phi_b^0$ to values much less than the bandgap energy (Kurtin *et al.*, 1969; Sze, 1981; Rhoderick, 1988). If true, limitations on the achievable energy conversion efficiencies of photoelectrochemical cells would be severe and rule out any practical advantage of using semiconductor/liquid junctions. However, in 1980, a research group at Bell Laboratories demonstrated an efficient, unpinned p -InP/ $V^{3+/2+}$ aqueous-based photoelectrochemical cell. In this system, the many oxidation states of vanadium cations (V^{5+} – V^{4+} – V^{3+} – V^{2+}) in HCl(aq.) allowed $U(A/A^-)$ to be varied over a 600 mV range by titrating in either $O_2(g)$ or dissolved Zn (Fig. 9.3; Heller *et al.*, 1981b). As the solution redox potential was varied, linear changes in ϕ_b^0 were observed from linear changes in V_{oc} . As shown in Fig. 9.3, V_{oc} changed linearly with an approximate slope of -1 , in accordance with eq. 9.1. Soon thereafter, the same group demonstrated an analogous correlation of V_{oc} and $U(A/A^-)$ at p -Si photoelectrodes in the same aqueous electrolyte (Heller *et al.*, 1981a), thus proving that 'unpinned' semiconductor/liquid junctions could be obtained for a variety of common materials. However, the poor efficiencies observed for the system

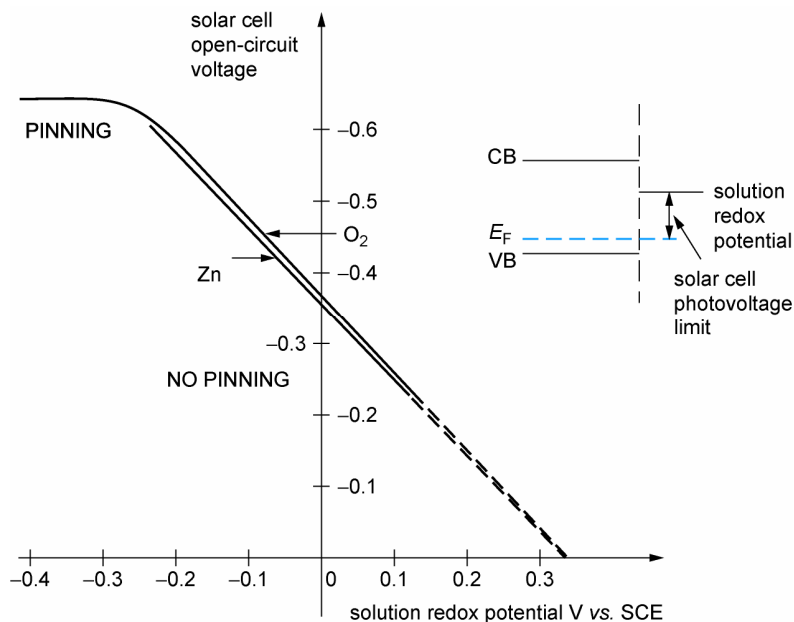


Figure 9.3 Variation of the open-circuit voltage of the $p\text{-InP}/V^{n+/(n-1)+}$, HCl/C cell with the redox potential of the solution. The electrochemical potential of the solution is made more positive by bubbling O_2 or more negative by dissolving Zn.

involving $p\text{-Si}$ also illustrated that the kinetics of interfacial charge transfer strongly influence the overall cell efficiencies, even if ϕ_b^0 is optimal.

Charge-transfer kinetics In early literature, ϕ_b^0 was the expected value of V_{oc} for an illuminated semiconductor/liquid junction that behaved ideally (Schneemeyer and Wrighton, 1979; Aruchamy and Wrighton, 1980; Tanaka *et al.*, 1981; Baglio *et al.*, 1982; Lin *et al.*, 1982; Baglio *et al.*, 1983). However, careful study of unpinned Si/liquid contacts demonstrated that the maximum V_{oc} obtainable for even unpinned photoelectrochemical cells is always less than ϕ_b^0 and is ultimately limited by kinetics rather than by thermodynamic factors (Lewis, 1984; Lieber *et al.*, 1984; Rosenbluth *et al.*, 1984). The observed charge-transfer rate across an n -type semiconductor/liquid interface is a function of the respective rates of all the possible kinetics processes, as enumerated in Fig. 9.4. Recombination of the photogenerated electron-hole pairs can occur in the bulk semiconductor (i_{br}), in the depletion region (i_{dr}), and at surface states (i_{ss}). Excited electrons can also either cross the junction barrier by thermionic emission (i_{te}) or tunnel through it (i_t) to reduce A in the solution. These five processes

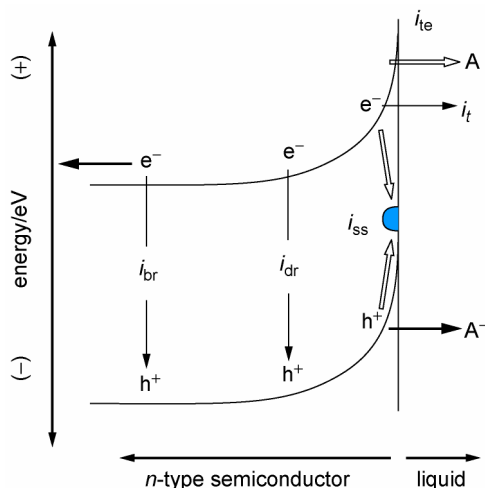


Figure 9.4 Recombination pathways of photogenerated charge carriers in an *n*-type semiconductor-based photoelectrochemical cell. The electron–hole pairs can recombine through a current density in the bulk of the semiconductor, i_{br} , the depletion region, i_{dr} , or through defects (trap states) at the semiconductor/liquid interface, i_{ss} . Charges can also tunnel through the electric potential barrier near the surface, i_t or can transfer across the interface, i_{te} . The bold arrows indicate the favourable current processes in the operation of a photoelectrochemical cell. The hollow arrows indicate the processes that oppose the excess of charge carriers generated by light absorption.

counteract the photogeneration of excess free charge carriers, and limit the achievable energy-conversion efficiency of a photoelectrochemical system. The relative influences of i_t and i_{te} can be suppressed by maximising ϕ_b^0 . If i_{dr} and i_{ss} can be sufficiently mitigated, then i_{br} will determine the largest possible photovoltage at a semiconductor/liquid junction. Under such conditions, the open-circuit voltage is given by eq. 9.2 (Lewis, 1984)

$$V_{oc} = \frac{kT}{q} \ln \left[\frac{i_{sc}}{i_o} \right] \cong \frac{kT}{q} \ln \left[\frac{i_{sc} L N_D}{q D n_i^2} \right] \quad (9.2)$$

where i_o is the dark saturation current density opposing the photogenerated current density (equal to i_{br} in this limiting case), i_{sc} is the photocurrent density at short circuit, L and D are respectively the diffusion length and diffusion coefficient of the minority charge carrier, N_D is the dopant density of the bulk semiconductor, and n_i is the intrinsic carrier concentration in the semiconductor. Since recombination of charge carriers in the bulk is always non-zero, the largest obtainable V_{oc} will always be less than ϕ_b^0 and is bound by eq. 9.2 for a given illumination intensity.

The rate of interfacial charge transfer can also restrict the efficiency of a photoelectrochemical system. For *n*-type semiconductor/liquid interfaces, the current density–potential relationship at forward bias can be analysed to extract the charge-transfer rate constant (Lewis, 2005)

$$\ln i(U) = \ln(-qk_{\text{ct}}[A]N_{\text{D}}) + \frac{q(U_{\text{fb}} - U)}{kT} \quad (9.3)$$

where $i(U)$ is the potential-dependent current density, k_{ct} is the interfacial charge-transfer rate constant, $[A]$ is the concentration of oxidised species in solution, U_{fb} is the potential where the band bending is zero, and U is the applied potential. Equation 9.3 offers a good check of the semiconductor/liquid interface charge-transfer properties, as a plot of $\ln i(U)$ vs. U should be linear with a slope of 0.026 V^{-1} at $T = 298 \text{ K}$ and should shift by 0.059 mV with each decade of change in $[A]$. Often, adsorption of redox species, occurrence of surface states, and/or surface corrosion and oxidation processes give plots of $\ln i(U)$ vs. U with slopes and/or shifts with $[A]$ that are significantly different from what is predicted by eq. 9.3. The difficulties in rigorously eliminating these effects have historically impeded quantitative analysis of interfacial charge-transfer rates at semiconductor/liquid junctions. In fact, although redox processes at semiconductor interfaces have received attention since the early 1960s (Freund and Morrison, 1968; Sparnaay *et al.*, 1969; Gerischer, 1969a, 1969b, 1973, 1977, 1984, 1987), a full set of comprehensive and self-consistent k_{ct} measurements has only recently been obtained for semiconductor/liquid junctions (Fajardo and Lewis, 1997; Hamann *et al.*, 2005a, 2005b, 2006).

Equation 9.3 also indicates an important aspect of charge transfer at semiconductor interfaces. Unlike metallic electrodes, electron transfer at ideally behaving *n*-type semiconductors occurs from a single electronic level, E_{c} (Bard and Faulkner, 1980). Consequently, the standard driving force for charge transfer, $-\Delta G^{\circ'}$, at *n*-type semiconductors is described by eq. 9.4 (Hamann *et al.*, 2005b)

$$-\Delta G^{\circ'} = -qU^{0'}(A/A^-) - E_{\text{c}} \quad (9.4)$$

where $U^{0'}$ is the formal potential for the A/A^- redox couple and E_{c} is the energy of the conduction-band edge. According to the classical Marcus–Gerischer models of interfacial charge transfer (Marcus, 1959, 1963; Gerischer, 1969a), the measured charge-transfer rate constant has a complex dependence on $-\Delta G^{\circ'}$, as shown by eq. 9.5 (Bard and Faulkner, 1980; Hamann *et al.*, 2005b)

$$k_{\text{ct}} = k_{\text{ct,max}} \exp \left[-\frac{(\Delta G^{\circ'} + \lambda)^2}{4\lambda kT} \right] \quad (9.5)$$

where $k_{\text{ct,max}}$ is the maximum rate constant observed at the optimum value of $-\Delta G^{\circ'}$, and λ is the reorganisation energy involved with a change in the nuclear configurations of the solvated species A and A^- . As discussed in more detail in Chapter 4, two important predictions about interfacial charge transfer are contained in eq. 9.5. First, the Marcus–Gerischer model of charge transfer predicts that when $-\Delta G^{\circ'}$ is equal to λ , the system is optimised for undergoing the maximum rate of charge transfer. Correspondingly, for values of $-\Delta G^{\circ'}$ that are much smaller, or much larger, than λ , the rate of charge transfer decreases significantly. Operationally, values of $\ln k_{\text{ct}}$ should show a parabolic dependence on $-\Delta G^{\circ'}$, in which $\ln k_{\text{ct}}$ will be small at both small and large values of $-\Delta G^{\circ'}$ (Hamann *et al.*, 2005b). Second, for $-\Delta G^{\circ'} < \lambda$ the Marcus–Gerischer model of charge transfer predicts that for a series of redox couples with the same thermodynamic driving force, the charge-transfer rate constants at the semiconductor/liquid junction will decrease with increasing values of λ .

A full test of these predictions regarding charge transfer at semiconductor electrodes in aqueous solutions requires a large-bandgap semiconductor that behaves in accord with eq. 9.3 and that resists surface-fouling processes. Non-degenerately doped ZnO satisfies both of these requirements (Morrison, 1980; Hamann *et al.*, 2005b). In 2005, charge-transfer measurements on aqueous *n*-ZnO/liquid junctions were reported for several different solutions that contained non-adsorbing, one-electron, outer-sphere redox couples with values of $-qU(A/A^-)$ that spanned the entire bandgap energy of ZnO. Figure 9.5 shows the dependence of k_{ct} on $-\Delta G^{\circ'}$ at *n*-ZnO, for a series of Os^{3+/2+} complexes with an average λ value of 0.64–0.69 eV. Values of k_{ct} measured over a 1.2 eV range of $-\Delta G^{\circ'}$ values exhibited the predicted parabolic shape with a clear ‘inverted’ region (*i.e.* decreasing values of k_{ct} for larger standard driving forces past the optimal exoergicity), heretofore not directly seen for any electrode charge-transfer process (Bard and Faulkner, 1980; Hamann *et al.*, 2005b). In agreement with the Marcus–Gerischer model, the largest k_{ct} values occurred for values of $-\Delta G^{\circ'}$ close to the (separately measured) λ values. Similarly, as seen in Fig. 9.6 for assorted Co^{3+/2+}, Ru^{3+/2+} and Os^{3+/2+} complexes, the experimental data agree quite well with the second prediction from eq. 9.5, which is that λ strongly determines the rate of charge transfer for a given thermodynamic driving force.

In Fig. 9.6, the four redox couples all have roughly equivalent nernstian solution potentials, but their λ values span a range of ~1 eV. The differences in λ result in measured charge-transfer rates that differ by almost a factor of 1000 even though the

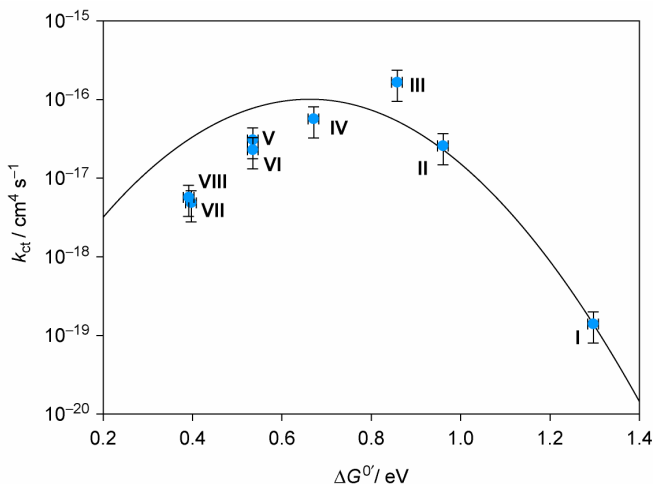


Figure 9.5 Plots of the electron-transfer rate constant for several $\text{Ru}^{3+/2+}$ and $\text{Os}^{3+/2+}$ compounds as a function of the standard driving force, $-\Delta G^0 = qU^0(A/A') - E_c$. The solid line represents the predicted k_{et} versus $-\Delta G^0$ behaviour for $k_{et,\text{max}} = 1 \times 10^{-16} \text{ cm}^4 \text{ s}^{-1}$ and $\lambda = 0.67 \text{ eV}$. The redox couples are: **I** $[\text{Ru}(\text{bpy})_3]^{3+/2+}$, **II** $[\text{Os}(\text{terpy})_2]^{3+/2+}$, **III** $[\text{Os}(\text{bpy})_3]^{3+/2+}$, **IV** $[\text{Os}(\text{Me}_2\text{bpy})_3]^{3+/2+}$, **V** $[\text{Os}(\text{bpy})_2(\text{MeIm})_2]^{3+/2+}$, **VI** $[\text{Os}(\text{bpy})_2(\text{Im})_2]^{3+/2+}$, **VII** $[\text{Os}(\text{Me}_2\text{bpy})_2(\text{MeIm})_2]^{3+/2+}$, **VIII** $[\text{Os}(\text{Me}_2\text{bpy})_2(\text{Im})_2]^{3+/2+}$. Source: Hamann *et al.* (2005b).

standard driving force for each couple is nominally the same (Hamann *et al.*, 2005a). These collective measurements demonstrate that simple one-electron charge-transfer processes at semiconductor/liquid junctions are experimentally in accord with the Marcus–Gerischer model of interfacial charge transfer.

Inhibiting surface corrosion or oxidation Long-term operation of a photoelectrochemical cell is contingent on the stability of the photoelectrode, i.e. the photogenerated charge carriers must not substantially participate in surface-fouling corrosion or oxidation processes. For practical device operation on the timescale of ten years, the coulombic efficiency of the light-driven photochemical process must be much greater than 99.999%.² As noted above, for small-bandgap *n*-type semiconductors, this constraint was unrealisable for several decades.

² For a photocurrent output of 10 mA cm^{-2} , $3.2 \times 10^6 \text{ C cm}^{-2}$ are passed across the photoelectrochemical interface during ten years of operation. During this span, assuming a faradaic current efficiency of 99.9999% for the desired photoelectrochemical reaction, approximately 3×10^{-5} moles of electrons per cm^2 are free to participate in side corrosion or oxidation reactions. In the case of the 4-electron oxidation of

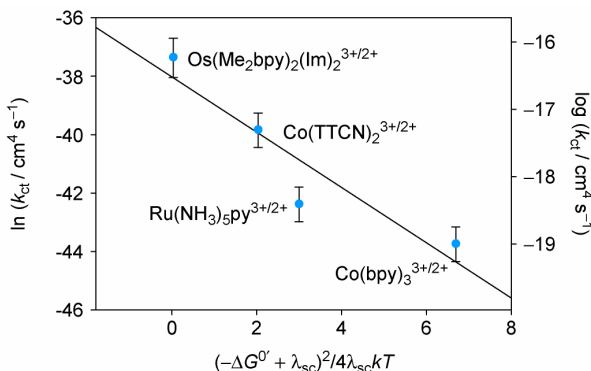


Figure 9.6 Plot of $\ln k_{ct}$ as a function of the quantity $(-\Delta G^0 + \lambda)^2 / (4\lambda kT)$ for several redox couples with $-\Delta G^0$ within a range of 0.5–0.6 eV. The solid line represents a linear least-squares fit of the data. Source: Hamann *et al.* (2005a).

A major breakthrough came in 1976, when three independent research groups explored the use of chalcogenide redox couples (X_2^{2-}/X^{2-} , where $X = S, Se, Te$) in regenerative cells employing n -type II–VI chalcogenide semiconductors (Ellis *et al.*, 1976; Hodes *et al.*, 1976; Miller and Heller, 1976). In this approach, the primary goal of the chalcogenide redox couples was not to maximise ϕ_b^0 or V_{oc} *per se*, but rather to alter the kinetics of the deleterious surface reactions. For example, the corrosion of CdS in aqueous solution occurs readily as a result of surficial (*i.e.* surface-bound) CdS-based S atoms oxidising to form $S_{(s)}$. However, the oxidation current for dissolved S^{2-} effectively competes with the surface oxidation process, preserving the CdS surface integrity and, correspondingly, the efficiency of the cell. As a technical success, this approach marked the first practical method for kinetically protecting thermodynamically unstable materials in working photoelectrochemical cells. Interestingly, the use of chalcogenide redox couples for stabilising semiconductors that do not themselves consist of chalcogenide atoms has also been reported. GaAs (Ellis *et al.*, 1977a; Gronet and Lewis, 1984), GaP (Ellis *et al.*, 1977a) and InP (Ellis *et al.*, 1977b) aqueous photoelectrochemical cells have all demonstrated improved performance through the use of X_2^{2-}/X^{2-} electrolyte contacts, although the mechanism(s) for the surface protection differs. Experimental data suggest that the X_2^{2-}/X^{2-} species chemisorb on the electrode surface and act as an interfacial charge-transfer catalyst rather than as sacrificial reductants (Bansal *et al.*, 1993).

Si to SiO_2 , this number of equivalents corresponds to the oxidation of approximately 5×10^{18} atoms of Si per cm^2 , *i.e.* an interfacial oxide layer with a thickness of roughly 5000 monolayers, or 15 μm .

Unfortunately, not only is the use of chalcogenide redox couples for stabilisation still limited to a small subset of semiconductor materials, but chalcogenide salts are toxic. In addition, this particular strategy limits the operation of such photoelectrodes to regenerative cells for a source of electrical energy, and not to produce fuel. A related scheme involves the use of $\text{Fe}(\text{CN})_6^{3-/4-}$ with CdSe electrodes (Noufi *et al.*, 1980; Rubin, 1985; Marcu and Strehblow, 1991; Seshadri *et al.*, 1991). In this system, $\text{Fe}(\text{CN})_6^{3-/4-}$ coordinates with the surficial Cd atoms, thereby preventing surface corrosion and, as shown in Table 9.1, resulting in a favourable efficiency (Arent *et al.*, 1992). Other lamellar chalcogenide semiconductors have similarly demonstrated inhibited corrosion in aqueous solutions that contain either I_3^-/I^- , Cl_2/Cl^- , or Br_2/Br^- , although the protective mechanisms in these systems are not fully understood.

A later study (Pomykal *et al.*, 1995) involving Si photoelectrodes in water/methanol mixtures elucidated the stabilising capacity of outer-sphere redox couples more fully. Three outer-sphere redox couples with nominally equivalent standard potentials, but varying reorganisation energies λ were separately used in photoelectrochemical cells with *n*-Si. Under illumination the amount of surface oxidation at *n*-Si electrodes tracked with the charge-transfer kinetics of the associated stabiliser. Specifically, as λ increased, the protecting capacity of the redox couple lessened and surface oxidation of *n*-Si increased, even though the solution potential, *i.e.* $-\Delta G^\circ$, in the three systems remained constant. Operationally, smaller values of λ translated to faster rates of charge transfer that allowed the redox couple reaction to compete kinetically with surface oxidation reaction(s).

9.3 Non-aqueous solvents

The instability of small-bandgap materials under illumination in water has been known for at least half a century. Still, the allure of electrochemical water splitting with semiconductors focussed research for several decades on aqueous systems. In fact, it was not until the late 1970s that researchers began to utilise non-aqueous solvents in the study of semiconductor/liquid junctions (Frank and Bard, 1975; Bolts and Wrighton, 1978; Yeh and Hackerman, 1978). With larger potential windows and far less corrosiveness than water, non-aqueous solvents such as acetonitrile, methanol and ethanol allowed researchers to determine whether most common semiconductors could in fact be useful as photoelectrodes or whether the same performance-limiting junction properties in analogous solid-state Schottky devices were operative. Perhaps more importantly, and in contrast to some of the seemingly *ad-hoc* protocols in aqueous systems, careful and systematic variation of the solution redox couple in

organic solvents afforded insight into the fundamental physics and chemistry of interfacial charge transfer at semiconductor electrodes.

In 1977, researchers at the Massachusetts Institute of Technology demonstrated stable photoelectrochemical cells with *n*-Si in ethanol-ferrocene^{0/+} systems, in contrast to the rapid degradation of Si electrodes in water (Legg *et al.*, 1977). Since that report, almost all other 'common' small bandgap semiconductors have been used to make stable, long-lasting non-aqueous photoelectrochemical junctions (Rosamilia and Miller, 1985; Severeyn and Gale, 1986; Kobayashi *et al.*, 1991; Mishra and Osseasare, 1992; Abshire and Richmond, 2000). A second milestone result was reported in 1984. That work demonstrated that high-quality, sustainable photoelectrochemical cells could be constructed with either *n*-Si or *p*-Si, with such systems exhibiting solar energy conversion efficiencies of 10–14% (Gibbons *et al.*, 1984; Lieber *et al.*, 1984; Rosenbluth *et al.*, 1984). These efficiencies far surpassed those of the best aqueous Si photoelectrochemical cells or the best Si/metal photovoltaics, and were comparable to those of solid-state diffused-junction solar cells (Lieber *et al.*, 1984). These same researchers demonstrated that Si interfaces in methanol and acetonitrile solutions were of such high electrical quality that the observed photoelectrochemical cell efficiency limitations reflected the materials properties of the bulk Si (Lieber *et al.*, 1984). In effect, they showed that the electronic quality of semiconductor/liquid junctions under illumination could equal or surpass that of more expensive solid-state *p*–*n* junctions.

Electrochemical measurements without illumination further demonstrated the ideal nature of many non-aqueous semiconductor/liquid junctions. For example, ϕ_p^0 values for many non-aqueous semiconductor/liquid junctions are directly sensitive to $U(A/A^-)$. In non-aqueous solvents, InP (Kohl and Bard, 1979; Heller *et al.*, 1981b; Pomykal *et al.*, 1996), Si (Fajardo *et al.*, 1995; Fajardo and Lewis, 1997) and GaAs (Casagrande *et al.*, 2000) have all exhibited partial or ideal sensitivities of ϕ_p^0 with changes in the solution potential in non-aqueous solvents. The earliest demonstrations of fully 'unpinned' non-aqueous semiconductor/liquid junctions were between *n*-Si or *p*-Si and a homologous series of ferrocene-based redox couples, as shown in Fig. 9.7 (Lewis, 1984). The ease of preparation, and technological importance, of Si electrodes prompted more in-depth analysis of the associated interfacial charge-transfer properties in these non-aqueous solvent systems. The measured rate constants k_{ct} for charge transfer at *n*-Si electrodes in methanol were consistent with those predicted by the Marcus–Gerischer model (Fajardo and Lewis, 1996), foreshadowing the later studies with ZnO. Although the small bandgap of Si precluded a full investigation of the driving-force dependence on k_{ct} , these researchers were able to establish an upper limit of $\sim 10^{-17} \text{ cm}^4 \text{ s}^{-1}$ for k_{ct} values at semiconductor/liquid junctions with outer-

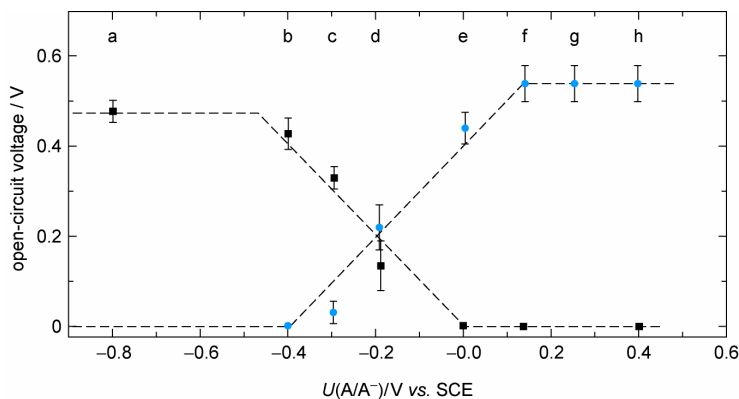


Figure 9.7 Open-circuit photovoltage vs. solution redox potential for *n*-Si and *p*-Si photoelectrodes in 1.0 M KCl/CH₃OH solution. The redox couples used were: (a) cobaltocene⁺⁰, (b) N,N'-dimethyl-4,4'-bipyridinium dichloride^{2+/+}, (c) N,N'-dibenzyl-4,4'-bipyridinium dibromide^{2+/+}, (d) decamethylferrocene^{0/+}, (e) N,N,N',N'-tetramethylphenylenediamine⁺⁰, (f) dimethylferrocene⁺⁰, (g) ferrocene⁺⁰, and (h) acetylferrocene⁺⁰. A tungsten-halogen bulb was used to provide light intensities which yielded short-circuit photocurrent densities of 25–30 mA cm⁻². Source: Lewis (1984).

sphere, one-electron redox couples. These data served as an important benchmark for interpreting and understanding interfacial charge-transfer rates at semiconductor electrodes (Pomykal *et al.*, 1996).

A final note should be made regarding room-temperature molten salts, *i.e.* ionic liquids, as special non-aqueous solvents. As shown in Table 9.1, ionic liquids have been used as the solvent system in regenerative photoelectrochemical cells employing semiconductors such as GaAs (Singh *et al.*, 1980a, 1980b; Rajeshwar *et al.*, 1981; Singh and Rajeshwar, 1981; Singh *et al.*, 1981; Thapar and Rajeshwar, 1982; Thapar and Rajeshwar, 1983), InP (Thapar *et al.*, 1982) and Cu₂O (Tachibana *et al.*, 2006). While the reported conversion efficiencies are noticeably poor for these particular systems, ionic liquids are still attractive due to their low toxicities, good chemical stabilities and ultra-low volatilities (Hagiwara and Lee, 2007). In particular, the latter two features of ionic liquids represent significant advantages over conventional non-aqueous solvents such as acetonitrile or methanol. Such organic solvents tend to either dry out and/or chemically degrade, two serious device-end problems that have limited, to date, the commercialisation of dye-sensitised nanocrystalline TiO₂-based cells (Figgemeier and Hagfeldt, 2004; Sommeling *et al.*, 2004) in such solvents.

9.4 Chemical modification of semiconductor surfaces

While the light absorption properties of a semiconductor are a function of its bulk properties, the nature of the semiconductor surface dictates the physical, chemical and electrical properties of the junction with the solution. As yet, no known semiconductor material natively demonstrates ideal interfacial behaviour at all times in all regenerative cell designs under all conditions. However, deliberate chemical modification of known semiconductor surfaces can both improve specific interfacial charge-transfer rates and impede some corrosion and oxidation processes. Three such approaches are particularly effective: (a) coating the semiconductor surface with thin metal films; (b) exposing the surface to chemical adsorbates; and (c) covalently grafting chemical groups to the semiconductor surface. These three tactics are detailed in this section.

9.4.1 Metallisation of the surface

Buried Schottky junctions An early strategy for protecting a semiconductor surface from photodegradation was to coat the solid with a continuous film of a noble metal or conducting polymer (Nakato *et al.*, 1975; Menezes *et al.*, 1980; Noufi *et al.*, 1981; Nakato and Tsubomura, 1985a). In these systems, the solution is in contact only with the outer metal(polymer), and the light-sensitive junction is buried on the underside of the metal(polymer) film. In fact, these systems have no direct semiconductor/liquid junction. Several issues are inherent to this design. The most serious one is that such a system is electrically equivalent to a circuit consisting of a Schottky diode wired in series to a physically separate, conventional, electrochemical cell (Harris *et al.*, 1977; Wilson *et al.*, 1977; Kumar and Lewis, 1991). In such a configuration, the electrolyte solution containing the redox couple in the electrochemical cell plays no role in facilitating or affecting the light-harvesting capacity of the conventional Schottky junction, other than to add a (relatively) high and efficiency-sapping contact resistance. Further, the light-harvesting capacities of such hybrid systems are limited by the properties of the solid-state semiconductor/metal(polymer) junction, which show strong Fermi-level pinning and often physical instability (in the case of polymers) (Rhoderick, 1988; Sailor *et al.*, 1990a, 1990b). Finally, smooth, coherent thick metal films absorb and/or reflect significant fractions of the incident light, further minimising the efficiency of such systems. If the metal film overlayer could be made uniformly thin ($\sim 10^9$ m) so that electrons (holes) could travel through to the solution ballistically, and the film did not reflect substantial amounts of incident light,

then perhaps $U(A/A^-)$ might play a role in determining ϕ_b° . However, this behaviour requires that the underlying semiconductor/metal junction is unpinned, which has yet to be demonstrated experimentally in most full semiconductor/metal systems.

Discontinuous, thin metal films Although coherent, thick metal films on semiconductors have not proved to date to offer a useful solution for improving photoelectrochemical systems, there are advantages to coating a semiconductor surface with a discontinuous, thin particulate metal film. Transition metal particles can facilitate complex, multi-step, fuel-forming reactions, such as water splitting, by decreasing or eliminating the required overpotential. In this way, the metal catalyst particles do not physically block the surface from undesirable oxidation/corrosion, but can still enhance the surface stability by improving the faradaic efficiency for the desired fuel-forming process relative to any deleterious side reactions. For example, deposition of dispersed, sub-micron-sized platinum particles on *p*-Si electrodes greatly increased the interfacial photoreduction of aqueous protons without apparent pinning of the *p*-Si/solution junction (Bocarsly *et al.*, 1980; Yae *et al.*, 2001). In fact, researchers at Bell Laboratories demonstrated that films of metal colloids (primarily Pt-type transition metals) not only enhanced electrochemical processes but did so without significantly attenuating the flux of photons reaching the semiconductor (Heller *et al.*, 1985; Porter *et al.*, 1985). In particular, decoration of *p*-InP with Pt clusters, via electrochemical reduction of PtCl_6^{2-} , dramatically increased the observed cell efficiency for proton reduction (Fig. 9.8). Similar activity enhancements from thin metal particulate films have been observed for Si (Yae *et al.*, 2001), GaP (Wilson *et al.*, 1977), TiO_2 (Nakato *et al.*, 1982; Nakato and Tsubomura, 1985b) and GaAs (Allongue *et al.*, 1992).

The nature of metal contacts at the semiconductor surface was not understood for quite some time. In principle, the same problem as with full semiconductor/metal contacts, Fermi-level pinning, should apply to these systems as well (Sze, 1981; Rhoderick, 1988). Further, metal contacts can act as sites that induce surface recombination (Rotondaro *et al.*, 1996). Hence, while metal particles should improve the interfacial charge-transfer kinetics, the presence of semiconductor/metal contacts at the surface should simultaneously limit the obtainable photovoltages and energy-conversion efficiencies. For Schottky-junction photovoltaics, even high-work-function metals form non-optimal junctions that possess a low ϕ_b° (Sze, 1981). Even if the solution is in direct contact with most of the semiconductor surface, the areas that are covered with the lower barrier metal/semiconductor contacts should still determine the field generated within the semiconductors, assuming the semiconductor/metal and semiconductor/liquid junctions operate independently and in

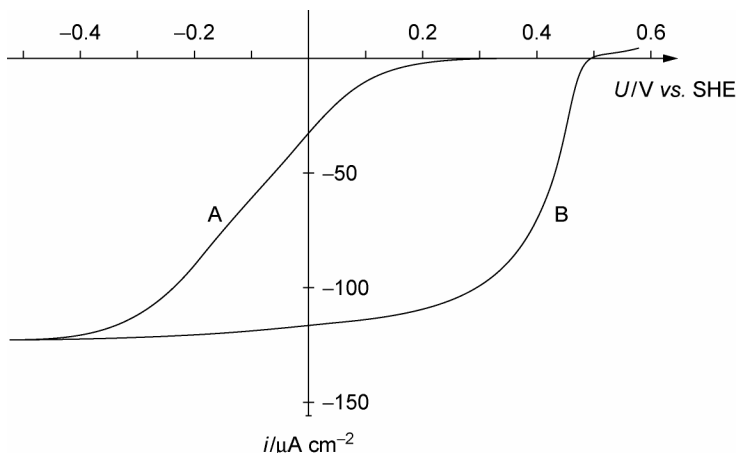


Figure 9.8 Current density–potential data for (A) *p*-InP and (B) *p*-InP (2.0 nm Pt) in 1.0 mol L⁻¹ HClO₄ under 888-nm illumination. The potential scan rate was 10 mV s⁻¹. Between -0.6 V and 0.4 V, the current densities approached a limit defined by the flux of photons entering the InP substrate. Source: Heller *et al.* (1985).

parallel. Simply, the current at the low barrier-height semiconductor/metal junctions should shunt charge transfer at the higher barrier-height semiconductor/solution contact regions, and the effective ϕ_b^0 at the surface should more closely reflect that of the semiconductor/metal junctions (Rossi and Lewis, 2001; Maldonado *et al.*, 2008). Studies at analogous inhomogeneous, solid-state Schottky junctions have suggested that in certain cases, ‘patches’ of junctions with different equilibrium junction barrier heights will not act independently, but junctions with higher ϕ_b^0 instead may screen, or ‘pinch-off’, the junctions with the lower ϕ_b^0 (Sullivan *et al.*, 1991; Tung, 1991; Tung *et al.*, 1991; Weiering *et al.*, 1996). While the ‘pinch-off’ effect has been widely assumed since the early 1980s to be operative for semiconductors decorated with finely-dispersed metal catalysts, only relatively recent work has actually tested the validity of this hypothesis in photoelectrochemical systems. In this study, *n*-Si electrodes were decorated with precisely-sized, separated Ni particles at a fixed areal coverage, as shown in Fig. 9.9 (Rossi *et al.*, 2000; Rossi, 2001; Rossi and Lewis, 2001). Ni particles were chosen because *n*-Si/Ni junctions are well known to possess low ϕ_b^0 values. The photoresponses of these and unmodified non-degenerately doped *n*-Si electrodes were measured in a dimethylferrocene⁺⁰ solution that formed a high ϕ_b^0 (~1 V) with bare *n*-Si (Fig. 9.10).

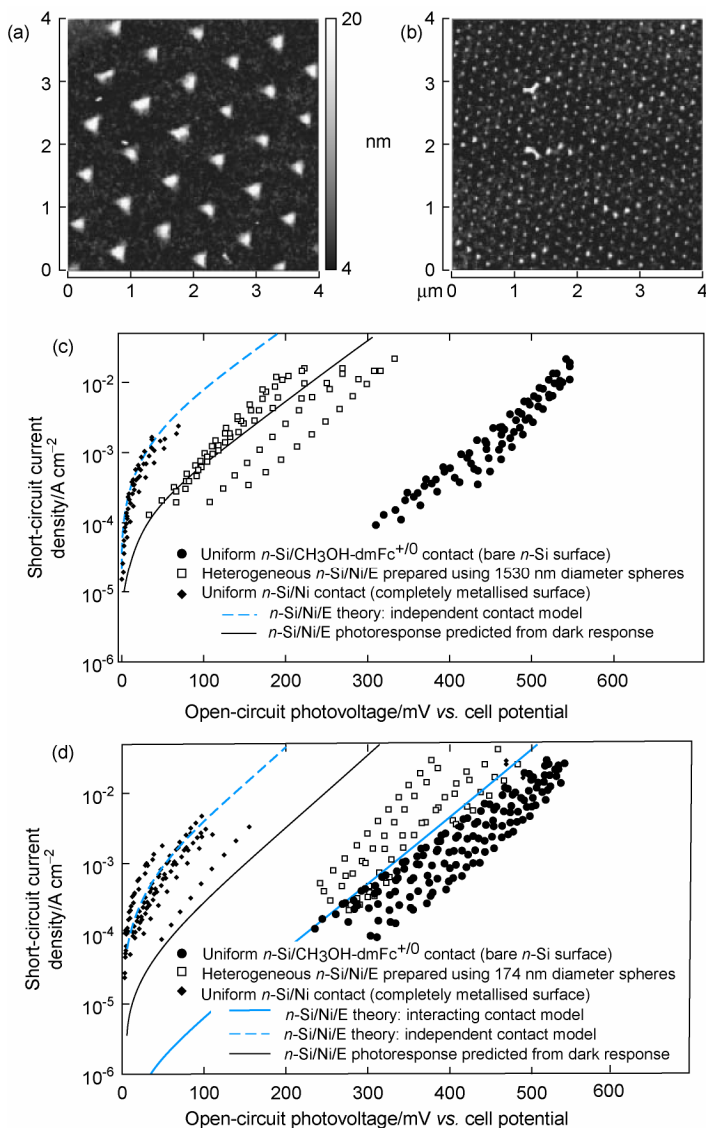


Figure 9.9 *n*-Si surface patterned with (a) 100 nm and (b) 25 nm Ni particle contacts; (c) Photoresponses of *n*-Si photoelectrodes modified with 25 nm Ni particles; (d) Photoresponses of an *n*-Si photoelectrode modified with 100 nm Ni particles. The predicted photoresponses are obtained from the barrier heights and non-ideality factors measured in the dark i - U responses. The solid blue curves indicate the predictions of the 'pinch-off' model and the blue dashed curves indicate the independent, parallel contacts model. Source: Rossi and Lewis (2001).

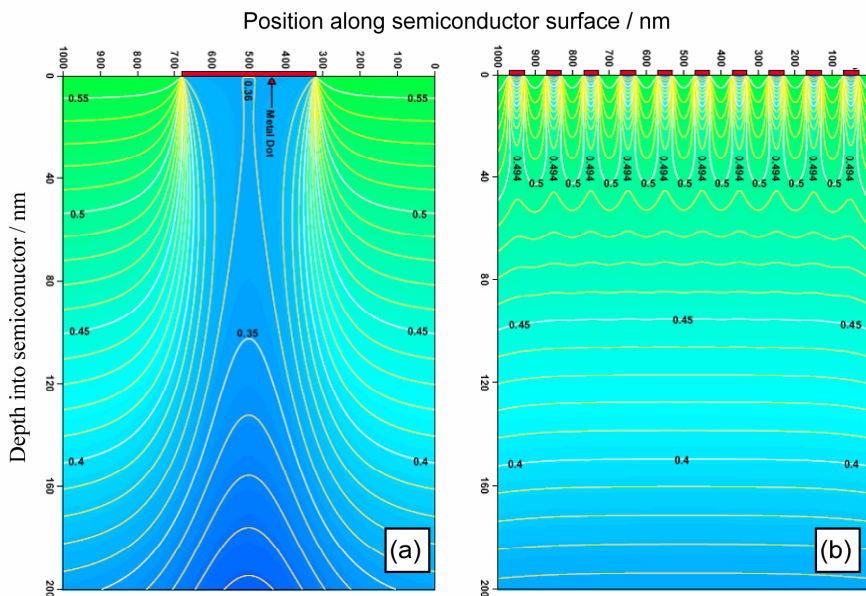


Figure 9.10 Equipotential contours within a semiconductor as a function of a low-barrier height nanopattern scale. Calculated equilibrium potential contours for non-homogenous barrier height interfaces, based on the ‘pinched-off’ model and the assumption of simple superposition of the electric potential perturbations. The model surfaces consist of metal disks of radius R_0 , spaced $5R_0$ apart, where (a) $R_0 = 180$ nm and (b) $R_0 = 20$ nm on a $6.14 \Omega\text{-cm}$ resistivity n -type Si substrate, with a doping density of $7.2 \times 10^{14} \text{ cm}^{-3}$, at 298 K. Source: Rossi (2001).

The ‘pinch-off’ model suggests that for surfaces with large, closely-spaced metal particles, the effective ϕ_b^0 for the entire interface will be dominated by the value of ϕ_b^0 for the metal/semiconductor contact. Conversely, for surfaces with metal particles having diameters and spacings less than the depletion width induced by the n -Si/dimethylferrocene $^{+/0}$ contacts (≤ 100 nm), the observed photoresponses should reflect the ϕ_b^0 of the semiconductor/dimethylferrocene $^{+/0}$ junction. The data from that study, shown in Figs. 9.9 and 9.10, agree with the model remarkably well, with surfaces having large Ni particles exhibiting poor photoresponses akin to the conventional, planar n -Si/Ni photodiodes, but with surfaces having small Ni particles demonstrating photoresponses almost as efficient as those at ‘plain’ n -Si/dimethylferrocene $^{0/+}$ junctions. This work represents some of the most conclusive evidence of the ‘pinch-off’ effect for metal-decorated photoelectrodes, and quantitatively supports the initial hypotheses suggested by the researchers at Bell Laboratories in the early 1980s.

9.4.2 Adsorption of solution species

For solid-state electronics, semiconductor surfaces are kept rigorously free of surface contaminants to prevent decreases in their electronic quality (Shulman and Wyluda, 1956). Interestingly, in photoelectrochemical applications, certain classes of surface adsorbates can greatly improve the quality and utility of semiconductor surfaces. As with metallisation approaches, two obvious benefits from surface adsorbates are formation of a protective blocking layer(s) and improved electrocatalysis of the desired charge-transfer kinetics. However, a third possible gain from the presence of adsorbates at semiconductor photoelectrodes is the mitigation of deleterious surface charge-carrier recombination stemming from chemically unsatisfied surface bonding. Although in many semiconductor/liquid systems the specific chemical nature(s) of interfacial charge-carrier trap sites is unclear, unsatisfied bonding orbitals of surface atoms are intrinsic (Shockley) surface states which can act as sites for recombination (Morrison, 1980). Specifically, atomic orbitals not involved in chemical bonds of surface atoms do not effectively overlap with their neighbours, appearing instead as discrete energy levels near the mid-bandgap level rather than contributing to the conduction and valence bands (Fig. 9.11). For many semiconductors, the deleterious effects of such surface states are not sufficiently alleviated during the polishing/cleaning/etching surface preparation steps.

Adsorbates that can bind specifically to electron-deficient or electron-rich ‘dangling’ surface atoms can, in principle, eliminate Shockley-type recombination sites. If the chemical interaction, *i.e.* bonding, between the surface atom and the adsorbate is sufficiently strong, the bonding and antibonding orbitals of the surface

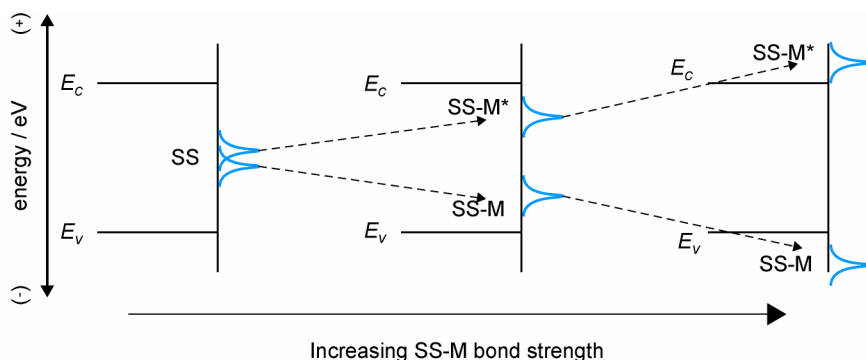


Figure 9.11 Depiction of an idealised chemical passivation of Shockley surface states. As the bonding strength between the surface and chemical group increases, the energies of the antibonding and bonding orbitals are shifted outside the bandgap.

atom-adsorbate 'complex' may push those traps outside of the bandgap at the surface, as illustrated in Fig. 9.11 (Heller, 1981). Although this argument has been used to promote the presence of beneficial surface oxides at certain small-bandgap electrodes, for example InP (Heller *et al.*, 1981b; Lewerenz and Schulte, 2002) and Si (Jakob *et al.*, 1991; Groner and Koval, 2001; Solares *et al.*, 2006), the preparation and characterisation of so-called 'good' oxides is still not well understood. The deliberate preparation (and associated features) of chemically/electrochemically generated surface oxides as a means for efficient surface modification are not formally discussed here. For Si oxides, the reader is directed elsewhere (Zhang, 2001). Nevertheless, the scheme outlined in Fig. 9.11 is not limited to surface oxide layers.

In practice, surface modification via physisorption/chemisorption entails immersing the electrode in a solution that contains a dissolved species. However, the protecting, catalytic and passivating influences of the specific adsorbates differ from case to case. Photoelectrochemical cells employing either InP or GaAs have demonstrated moderate to strong sensitivities towards cationic adsorbates, specifically metal cations (Heller *et al.*, 1983; Tufts *et al.*, 1987). In the case of small-grained, polycrystalline *p*-InP, brief soaks in aqueous solutions containing Ag^+ have led to substantial increases in the efficiency of $\text{V}^{3+}/\text{V}^{2+}$, HCl(aq) photoelectrochemical cells (Kim *et al.*, 1998). The reported rationale for the observed improvements was passivation of the grain boundaries by Ag-containing species. In more recent work, researchers at the Hahn-Meitner Institute suggest that improved InP interfaces in HCl are a result of adsorbed InCl(aq) species resulting from slight corrosion of the surface (Lewerenz and Schulte, 2002). These researchers indicate that the modified InP surface is more chemically inert towards further oxidation, and the band-edge energies remain favourable for photoelectrochemical processes. For *p*-GaP and *n*-GaAs, aqueous photoelectrochemical cells improve after adsorption of 'heavy' transition metal cations such as Ru^{3+} (Tufts *et al.*, 1989; Tan *et al.*, 1991), Co^{3+} (Tufts *et al.*, 1989; Tan *et al.*, 1991), Ir^{3+} (Tufts *et al.*, 1989), Rh^{3+} (Tufts *et al.*, 1989; Bansal *et al.*, 1993) and Os^{3+} (Tufts *et al.*, 1989; Tan *et al.*, 1991). In GaAs systems, the role of the metal cation is apparently to catalyse the interfacial rate of Se^{2-} oxidation. In fact, an *n*-GaAs electrode treated with Os^{3+} that demonstrated favourable properties in the aqueous $\text{Se}_2^{2-}/\text{Se}^{2-}$ system showed no enhancement as compared with an untreated *n*-GaAs electrode in a separate solvent/one-electron redox couple system (Fig. 9.12) (Tan *et al.*, 1991). Hence, the merits of these adsorbed cationic species are strongly system-dependent.

A different phenomenon involving metallic cation/surface interactions is photointercalation (Ang and Sammells, 1982; Rauh, 1982; Betz, 1985; Sharon *et al.*, 1991). For lamellar semiconductors under illumination, small cations can intercalate

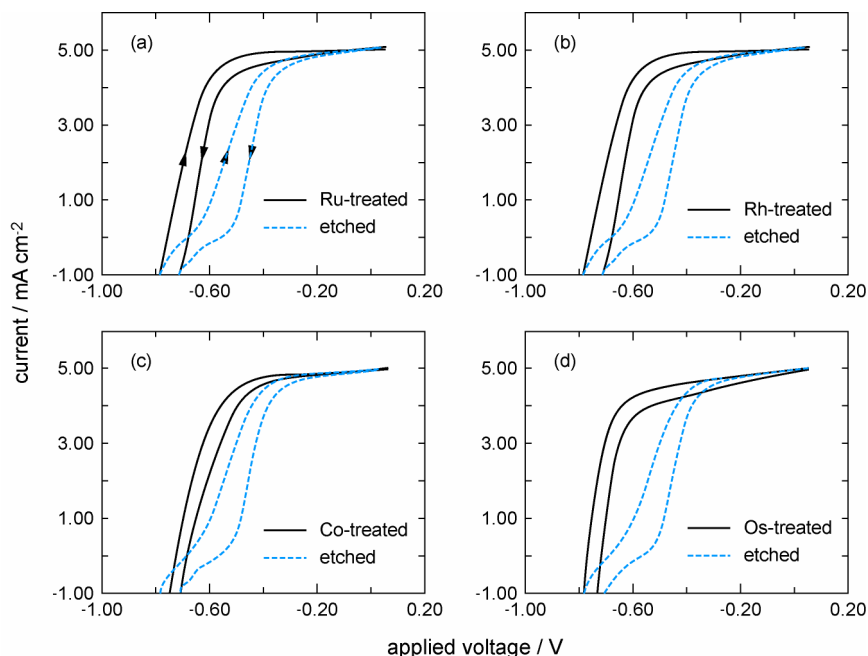


Figure 9.12 Current density–voltage properties of (100)-oriented n -GaAs electrodes in contact with aqueous KOH solutions containing the Se^{-2-} redox couple. In each measurement, the illumination intensity was adjusted to obtain a current density of 5.0 mA cm^{-2} at $+0.05 \text{ V}$ vs. the nernstian potential of the cell. The dashed line represents the i – U behaviour of an etched n -GaAs electrode in each experiment and the full line represents the i – U behaviour of a n -GaAs electrode soaked in (a) 0.010 M (pH 2.0) RuCl_3 , (b) 0.010 M (pH 2.0) RhCl_3 , (c) 0.010 M (pH 2.0) $\text{Co}(\text{NH}_3)_6\text{Cl}_3$, (d) 0.010 M (pH 2.0) OsCl_3 . The electrode was cycled between -0.85 and $+0.05 \text{ V}$ vs. the cell potential at 50 mV s^{-1} . Source: Bansal *et al.* (1993).

between the basal planes, in a process akin to the ion insertion process in Li-ion rechargeable batteries. In principle, such systems can operate as photoelectrochemical batteries, as discussed in Chapter 10, where the solar energy is stored and then discharged in the absence of light (Sharon *et al.*, 1991). However, the material's stability demands for consistent intercalation/de-intercalation have hampered development, and such systems have been little pursued since the mid-1980s (Akuto and Sakurai, 2001).

Nucleophilic adsorbates have also yielded interesting system improvements. Lamellar chalcogenides exhibit a strong sensitivity towards dissolved Lewis bases. For example, the photoelectrochemical behaviour of WSe_2 and MoSe_2 photoelectrodes dramatically improved after exposure to solutions that contained pyridines or ethylenediaminetetraacetic acid, respectively (Canfield and Parkinson, 1981; Fan

and Bard, 1981). These species are thought to make a nucleophilic attack on, and coordinate to, electron-deficient atoms that are exposed at step edges. The observed initial efficiency enhancements are significant, but gradually diminish over several days of continuous operation. Exposure of GaAs photoelectrodes to solutions with chalcogenide-containing anions improved their current–voltage responses as well. The data suggest that the As atoms are particularly sensitive to these adsorbates, but there is debate regarding the specific chemistry. Chemisorption of thiol-containing organic compounds has been studied at *n*-InP (Gu and Waldeck, 1998), *n*-GaAs (Lunt *et al.*, 1991; Moumanis *et al.*, 2006; Voznyy and Dubowski, 2006; Rodriguez *et al.*, 2007) and *n*-CdX (X = S, Se) surfaces (Natan *et al.*, 1986; Thackeray *et al.*, 1986). For CdX, researchers at the Massachusetts Institute of Technology discovered that thiol adsorption in aqueous solutions strongly suppressed surface photooxidation over a wide range of pH values, and shifted the conduction/valence band edges at the surface by as much as 500 mV, as indicated in Fig. 9.13 (Natan *et al.*, 1986). While these changes produced by thiol adsorption are among the highest seen after any deliberate surface treatment, they were highly dependent on the specific thiol used. Both GaAs and InP also showed strong adsorption of alkyl thiols, but neither material has yet demonstrated comparable enhancements in their photoelectrode performance to the level exhibited by the CdX systems.

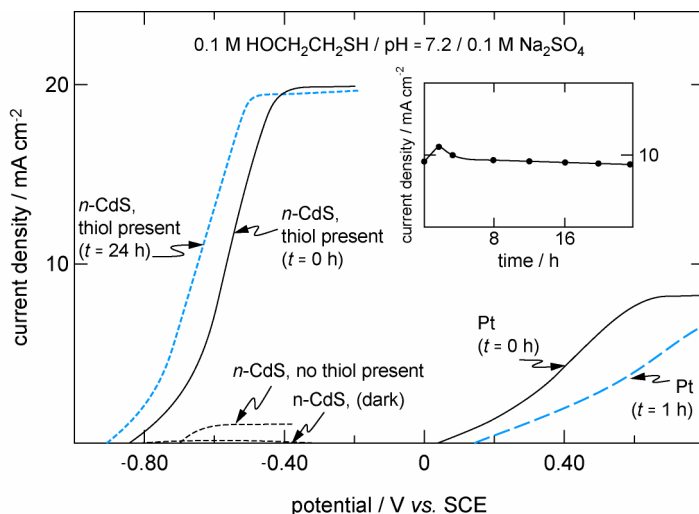


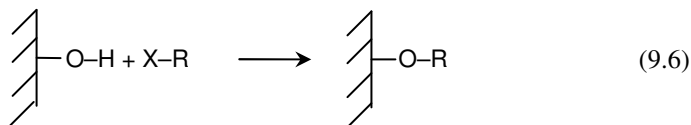
Figure 9.13 Steady-state photocurrent density–potential data (scan rate 5 mV s^{-1}) for *n*-CdS in 0.1 M 2-mercaptoethanol/0.1 M Na_2SO_4 at pH 7.2, initially and after 24 h of irradiation. The inset shows the current density obtained over the 24-h period. The excitation source was a tungsten-halogen lamp. Source: Natan *et al.* (1986).

9.4.3 Covalently-attached surface groups

Adsorption as a means to improve the behaviour of semiconductor interfaces is strongly system-dependent, and the benefits are generally short-lived. Additionally, the resultant surface properties after modification by adsorbates are difficult to predict *a priori*. To control semiconductor surfaces deterministically, and to impart long-lasting enhancements, several groups have pursued covalently grafting specific chemical functionalities to the semiconductor surface.

Reactions with surface oxides

Halide reactions The surface oxide of InP allows for facile chemical derivatisation of such electrodes. Researchers at the Massachusetts Institute of Technology, and later at the California Institute of Technology, demonstrated that the P-rich (111) face of InP could be controllably modified via coupling with organic halide compounds (Spool *et al.*, 1986; Sturzenegger *et al.*, 1999; Prokopuk and Lewis, 2004). The general approach capitalises on surface -P-OH bonds that are present under ambient conditions (Sturzenegger *et al.*, 1999). These bonds can be reacted according to eq. 9.6



where $\text{X} = \text{Br}, \text{Cl}, \text{or I}$ and $\text{R} = \text{any organic or silyl functionality}$. Near full monolayer coverages have been demonstrated by use of x-ray photoelectron and infrared spectroscopies. A nice demonstration of the power of halide surface modification has been shown through modification of InP surfaces with $\text{-CH}_2\text{C}_6\text{H}_5\text{CF}_3$ groups (Prokopuk and Lewis, 2004). This process shifted the band edges of *n*-InP ~ 100 mV closer to the vacuum-level energy. For *n*-InP, this shift resulted in a commensurate increase in the InP band bending in contact with solutions having electrochemical potentials that spanned a large range of $U(\text{A/A}^-)$, as shown in Fig. 9.14. In addition, the change in band-edge energies occurred without measurable change of the InP surface-recombination rate. As the surface-modification chemistry involves -POH groups, analogous effects should occur on the P-rich faces of other P-containing III-V semiconductors.

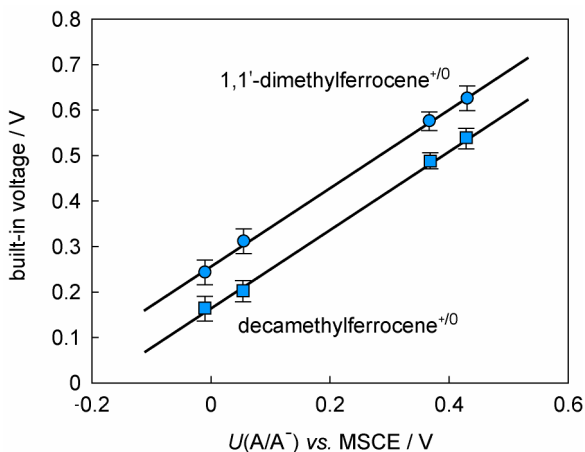
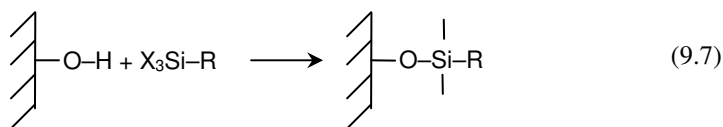


Figure 9.14 Dependence of the built-in voltage (U_{bi}) of (■) $n\text{-InP}$ and (●) $n\text{-InP-CH}_2\text{C}_6\text{H}_4\text{CF}_3$ electrodes on the Nernstian potential $U(A/A^+)$ of solution contacts with the one-electron, outer-sphere redox systems $1,1'\text{-dimethylferrocene}^{+/0}$ and $\text{decamethylferrocene}^{+/0}$. Nernstian potentials have been referenced with respect to a methanolic SCE. The mean U_{bi} value of every electrode/electrolyte contact was determined using at least 10 AC input voltage frequencies, and the means and standard deviations of these mean U_{bi} values for at least five separate electrodes are depicted at each value of $U(A/A^+)$. Linear regression for the two sets of data yields slopes of 0.85 and 0.86 for the etched and $\text{BrCH}_2\text{C}_6\text{H}_4\text{CF}_3$ -modified InP, respectively. Source: Prokopuk and Lewis (2004).

Silylation Researchers at the University of North Carolina first developed the practice of chemically modifying electrode surfaces through the coupling of alkyl silane compounds to surface hydroxyl groups, as in eq. 9.7 (Moses *et al.*, 1975).



where $\text{X} = \text{Cl}$ or OCH_3 , and R is an organic/organometallic functionality. The reaction scheme works not only for metal oxide materials, but for any surface having appreciable surface oxide. This method was soon adopted as a popular approach to modify silicon surfaces covered with native oxide layers. Attachment of short alkyl groups, however, resulted in little improvement in the quality and stability of $n\text{-Si}$ and $p\text{-Si}$ electrodes in aqueous solutions (Yoneyama *et al.*, 1980). Silylation proved a much more effective strategy if the surface group were itself redox-active (Bolts and Wrighton, 1978; Wrighton *et al.*, 1978; Bolts *et al.*, 1979; Tanaka *et al.*, 1981).

Through silylation, the redox-active groups could be electrically coupled to the semiconductor, and charge carriers could be rapidly shuttled from the semiconductor to the surface redox groups, acting as reaction mediators that effect redox reactions with dissolved species. In one notable case, a significant improvement in the stability of modified *n*-Si photoanodes in contact with aqueous $\text{Fe}(\text{CN})_6^{3-/4-}$ solutions was reported (Bolts *et al.*, 1979). In that work, photogenerated holes were shuttled to surface-bound ferrocene groups rapidly enough that the rate of surface photo-oxidation, relative to that at unmodified surfaces, was minimised. In this way, the lifetime of the *n*-Si interface in aqueous solution was extended by more than an order of magnitude (Fig. 9.15). In separate but related work, electrocatalysis was increased as a result of silylation of Si photoanodes and photocathodes with surface redox groups. For example, the interfacial reduction of ferricytochrome *c* was facilitated by surface-bound N,N'-dialkyl-4,4'-bipyridinium groups, to the extent that when the electrode was illuminated the rate of interfacial reduction of ferricytochrome *c* was limited by mass transport rather than by kinetics (Lewis and Wrighton, 1981).

Interestingly, although metal oxide semiconductor surfaces were among the first systems to support silylation functionalisation, relatively little has been demonstrated

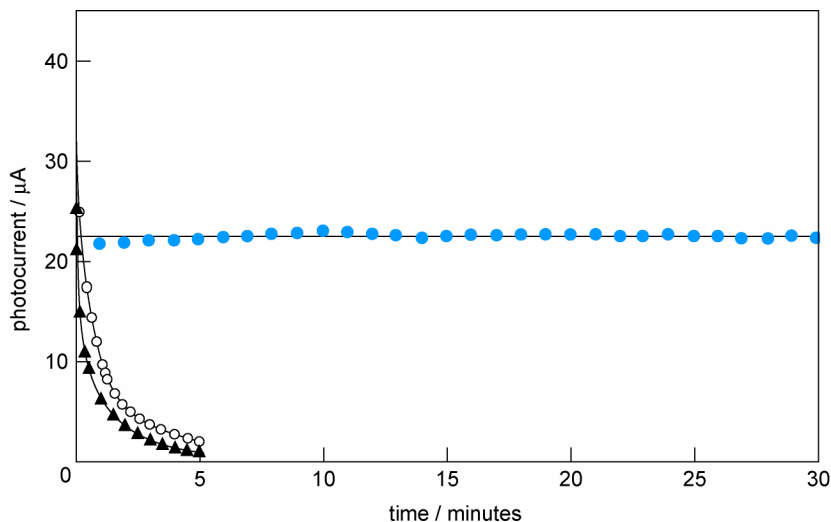


Figure 9.15 Plots of photocurrent against time for an *n*-Si electrode illuminated with 632.8 nm light at ~6 mW. The photoelectrode was held at +0.2 V vs. SCE in a stirred solution. The supporting electrolyte was 0.1 M NaClO_4 in doubly-distilled, deionised H_2O . Run 1(▲), HF-etched 'naked' electrode in supporting electrolyte only. Run 2(○), 'naked' electrode re-etched with HF, in supporting electrolyte plus 4×10^{-3} M $\text{Fe}(\text{CN})_6^{4-}$. Run 3(●), electrode derivatised with (1,1'-ferrocenediyl)dichlorosilane in the same solution as run 2. Source: Bolts *et al.* (1979).

in the way of improving, or even modulating, their interfacial properties by this method. Since the stability of many metal oxides as photoanodes in water is normally good (Finklea, 1988), work has instead focussed on manipulating the energies of the conduction/valence band edges. For example, the band edges of TiO_2 are known to depend on the crystal type of the material, with E_c and E_v at different energies for anatase surfaces than for rutile surfaces (Kavan *et al.*, 1996). For the former TiO_2 crystal type, E_c is favourable for the reduction of protons to $\text{H}_2(\text{g})$ but, for the latter crystalline phase, sustained H_2 evolution is not thermodynamically possible at 1 atm of $\text{H}_2(\text{g})$ because E_c is not sufficiently favourable.

Moreover, for all metal oxide semiconductors and for all small-bandgap semiconductors with appreciable surface oxides, the band-edge energies shift with solution pH (Hardee and Bard, 1975; Bolts and Wrighton, 1976; Watanabe *et al.*, 1976; Finklea, 1988; Gerischer, 1989). This phenomenon is generally attributed to the charge accumulated at the aqueous semiconductor/liquid junction from the activity of protons at the surface (Morrison, 1980). For these *n*-type semiconductors, the electrostatic charge accumulated at the interface acts as a net dipole that shifts E_c and E_v relative to the vacuum level. Hence, the bottom of the conduction-band and the top of the valence-band energies at the surface are related to the solution pH (in the absence of other adsorbing cationic/anionic species) by eq. 9.8 (Morrison, 1980)

$$E_c = E_c^\circ + \ln 10 \left[kT(\text{pH}_{\text{pzc}} - \text{pH}) \right] \quad (9.8)$$

where pH_{pzc} is the pH at which the net surface charge is 0 and E_c° is the conduction-band edge at the pH_{pzc} . In the absence of interfering adsorbates, eq. 9.8 implies that the surface band-edge energies shift by 0.059 V per unit pH at $T = 298$ K. Either eliminating the pH dependence of the band edges and/or shifting those band edges to more favourable levels are desirable goals in the development of water-splitting photoelectrochemical systems. In principle, if all of the surface $-\text{OH}$ groups could be replaced with $-\text{O}-\text{Si}-\text{R}$ groups, then the pH dependence of the band edges ought to be minimised, or even eliminated. Similarly, if the R group is basic, the pH dependence should change sign or, if the R group is strongly electron-donating/withdrawing, the band edges should shift accordingly (Vilan *et al.*, 2000; Cahen and Kahn, 2003). Unfortunately, for TiO_2 and SnO_2 (Finklea and Murray, 1979; Kabir *et al.*, 1981; Finklea, 1988), surface modifications with alkyl groups via silylation reactions have shown none of these effects. Researchers at Northwestern University have suggested that the pH dependence of metal oxides is more intimately associated with proton intercalation (Lyon and Hupp, 1999), indicating that the surface $-\text{OH}$ groups may not be as relevant to the pH dependence as commonly assumed. Whether the insensitivity

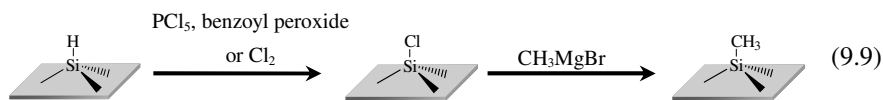
of silylation reactions to the band-edge energetics of many metal oxides supports the intercalation hypothesis or alternatively suggests an inability of the silylation reaction scheme to modify a sufficient fraction of the surface-based –OH groups in the systems studied to date is presently not fully elucidated.

Alkylation of covalent semiconductors

A limitation of surface functionalisation via silylation is the need for the prerequisite surface oxide. For group IV semiconductors such as Si or Ge, this requirement means that the starting surface will generally contain a high density of deleterious surface recombination sites. Rather than building on inherently electronically defective surfaces, surface reactions that involve freshly etched, ‘clean,’ oxide-free surfaces have been vigorously pursued. The most common approaches are extensions of known organic synthetic reactions for adding alkyl or aryl groups. In 1962, researchers at RCA (Amick *et al.*, 1962; Cullen *et al.*, 1962; Gerlich *et al.*, 1962) reported chemically grafting linear alkyl chains to Ge surfaces, the first report of deliberate modification of semiconductor surfaces through wet chemistry. However, for Ge surfaces, controlled, periodic surface atom bonding through chemical modification was (and still is) thwarted by the issues associated with the preparation of stable, clean, starting surfaces (Loscutoff and Bent, 2006). In contrast, cleaning and etching procedures for Si surfaces are much more well developed and understood (Blackwood *et al.*, 1992; Poate *et al.*, 1994; Roche *et al.*, 1994; Allongue *et al.*, 1995; Kaji *et al.*, 1995). Etching of Si(111) in basic aqueous fluoride solutions yields surfaces with large, atomically flat terraces, in which each atop Si atom is terminated by a single hydride group (Higashi *et al.*, 1990; Higashi *et al.*, 1991; Hines *et al.*, 1993). Although these monohydride-terminated Si(111) surfaces are quickly degraded in air and in water, they initially contain a low density of surface trap states (Yablonovitch *et al.*, 1986; Royea *et al.*, 2000; Yu *et al.*, 2006). Using carefully etched Si surfaces as starting platforms, several wet chemical approaches have recently been developed to functionalise Si(111) surfaces. Such methods include chlorination (Terry *et al.*, 1997a, 1997b, 1999; He *et al.*, 1998); alkylation by reacting the halogenated surface with Grignard reagents or with lithium alkyls (Bansal *et al.*, 1996; Terry *et al.*, 1997a); alkylation by olefin grafting induced by UV irradiation (Effenberger *et al.*, 1998; Boukherroub *et al.*, 1999; Boukherroub and Wayner, 1999; Cicero *et al.*, 2000; Lie *et al.*, 2002); alkylation by free-radical initiation (Linford and Chidsey, 1993; Linford *et al.*, 1995) or thermal activation (Linford *et al.*, 1995; Sung *et al.*, 1997; Sieval *et al.*, 1998); hydrosilylation of unsaturated hydrocarbons (Cicero *et al.*, 2000; Lehner *et al.*, 2003; Bocking *et al.*, 2004; Liu *et al.*, 2006); Diels–Alder

reactions (Teplyakov *et al.*, 1997, 1998); and electrochemical processes (Zazzera *et al.*, 1997; Allongue *et al.*, 1998; Boukherroub *et al.*, 1999).

The merits of the various routes to introducing alkyl groups to Si(111) surfaces depends on the intended application. In general, the kinetic stability of Si-C bonds relative to that of Si-H bonds affords enhanced oxidation resistance. For illustration, the enthalpies of formation of SiH_4 and $\text{Si}(\text{CH}_3)_4$ are $+32 \text{ kJ mol}^{-1}$ and -202 kJ mol^{-1} at $T = 300 \text{ K}$, respectively (Brimm and Humphreys, 1957; Lin *et al.*, 1996). Hence, SiH_4 is an unstable, reactive compound while $\text{Si}(\text{CH}_3)_4$ is a benign, moderately unreactive chemical. For surfaces, the bond dissociation energies for surface Si-H and Si-C bonding are estimated to be 323 and 369 kJ mol^{-1} , respectively (Buriak, 2002). For photoelectrochemical systems, the attached surface groups should mimic the ideal H-termination of etched Si(111) for effective protection against surface photodegradation. For Si(111) surfaces, the $3.8 \text{ \AA}$ separation between adjacent atop Si atoms thus puts a constraint on the size of the surface group (Nemanick *et al.*, 2006a). As a result, only $-\text{CH}_3$ (methyl) groups amongst saturated alkyl groups are capable of terminating every Si surface atom without suffering severe steric repulsion from neighbouring groups (Nemanick *et al.*, 2006b). A comparison of alkylating methods that allow introduction of $-\text{CH}_3$ groups suggests that the two-step chlorination-Grignard reaction scheme, eq. 9.9, is a very effective route for production of high quality, CH_3 -terminated Si(111) surfaces (Webb and Lewis, 2003).



Si(111) surfaces that have been ‘methylated’ (*i.e.* functionalised with $-\text{CH}_3$ surface groups) by this route have demonstrated outstanding oxidation resistance in air (Bansal *et al.*, 1996; Webb and Lewis, 2003) and have shown persistent and extremely low surface recombination velocities in air and in solution (Royea *et al.*, 2000). Recently, the observation of $-\text{CH}_3$ surface groups in direct registry with the underlying atop Si atoms following ‘methylation’ of Si(111) was reported (Fig. 9.16) (Yu *et al.*, 2005). The low-temperature STM data in this figure highlight the agreement between the predicted spacing and structure of a $-\text{CH}_3$ monolayer and the observed behaviour of Si(111) surfaces terminated with $-\text{CH}_3$ groups. Specifically, the centre-to-centre distance between the groups, and the torsional angle between neighbouring groups, are in accord with the known lattice spacings of Si(111) and the expected lowest-energy conformation of close-packed $-\text{CH}_3$ groups. This high surface coverage, and the stability of the Si-C bond, allows for long-lived and high-level

electrical perfection, even after several days in air. In fact, electrically-active defect-site densities of less than 1 in every 10^7 surface atoms are routinely produced (Royea *et al.*, 2000). Correspondingly, experiments with CH_3 -terminated n -Si(111) as photoanodes in aqueous $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solutions have demonstrated a marked suppression of surface photooxidation (Bansal and Lewis, 1998a, 1998b). Figure 9.17 contrasts the short-lived activity of unmodified n -Si(111) under illumination with the impressive stability of CH_3 -terminated n -Si(111) under the same illumination conditions.

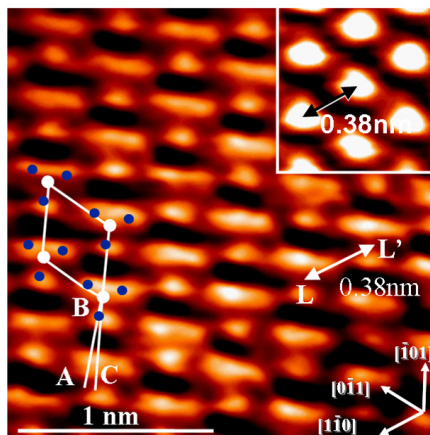


Figure 9.16 Scanning tunnelling microscopy (STM) image of CH_3 -terminated Si(111), collected at $T = 4.7$ K, at a sample bias of $V_s = -2.5$ V and at a constant current of 0.050 nA. The colour range (dark = low; bright = high) is 0.05 nm. The separation between the centres of the three bright spots, marked as line L-L', is 0.38 nm. The directions of the low-index planes of this crystal, as determined from X-ray crystallography, are indicated in the lower right. The drawn parallelogram represents the surface unit cell. Four $-\text{CH}_3$ group drawings are superimposed onto the image, assuming that the $-\text{CH}_3$ groups are in registry with atop Si atoms, to illustrate the position and relative orientation of $-\text{CH}_3$ groups. The angle formed between A, B, and C is $7 \pm 3^\circ$. (Inset) STM image, taken at $T = 77$ K on the same CH_3 -terminated Si(111) surface, revealing a series of triangularly-shaped bright regions in a 1×1 structure, with the spots separated by a distance of 0.38 ± 0.01 nm. Image size: 1 nm $\times$ 1 nm. No detailed structure in the bright spots was observed at this temperature. Source: Yu *et al.* (2005).

While the protective capacity afforded by surficial $-\text{CH}_3$ groups in Fig. 9.17 is substantial, it still needs to be improved for practical (*i.e.* tens of years) operation of Si photoelectrodes in aqueous photoelectrochemical cells. However, another important manifestation of surface properties imparted to Si by $-\text{CH}_3$ modification is the insensitivity of the values of E_c and E_v to changes in the pH of aqueous solutions (Hamann and Lewis, 2006).

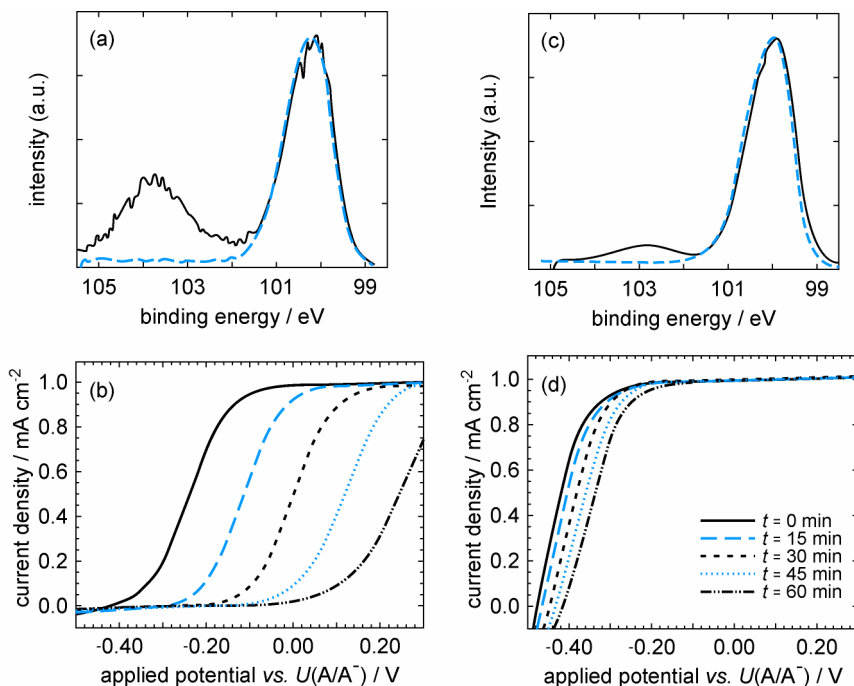


Figure 9.17 (a) High-resolution XP spectra of the Si 2*p* region of a H-terminated *n*-type Si(111) surface before and after immersion in 0.35 M K₄Fe(CN)₆–0.05 M K₃Fe(CN)₆ (aq) solution for 10 min under ambient conditions. The Fe(CN)₆^{3-/4-}-exposed surface showed approximately three monolayers of oxide, as evidenced by the area of the peak that occurred at 3.6 eV higher in binding energy than the bulk silicon 2*p* peak. (b) Time dependence of the *i*–*U* behaviour of an H-terminated Si electrode in contact with Fe(CN)₆^{3-/4-} (aq) solution under white-light illumination. (c) Representative high-resolution XP spectra of the Si 2*p* region of a CH₃-terminated *n*-type Si(111) surface. The oxide peak occurred 3.0 eV higher than the bulk Si 2*p* peak, and this surface showed less than one monolayer of oxidised Si. (d) Time dependence of the *i*–*U* behaviour of a –CH₃-terminated surface in contact with Fe(CN)₆^{3-/4-} (aq) solution as in (b). Source: Bansal and Lewis (1998b).

As discussed above, the acid/base equilibria of oxide surface groups impart a considerable pH-dependence to the band-edge energies of most semiconductors. However, the effective pK_a of C–H bonds in CH₃SiH₃ has been estimated to be ~34 (Durmaz, 1975). Assuming surficial –CH₃ groups on Si behave similarly, the methylated Si surface pK_a is then outside the conventionally obtainable pH ranges in aqueous solution. As predicted by Marcus–Gerischer interfacial charge-transfer theory, the standard driving force for interfacial charge transfer at a semiconductor to a pH-independent redox couple should change considerably as the pH is varied when

the band-edge energies shift with changes in solution pH. This behaviour is well known for many semiconductors and has been extensively analysed for n -ZnO (Hamann *et al.*, 2006). However, if the band-edge energies are insensitive towards solution pH changes, then the standard driving force, and observed charge-transfer rates, to the solution redox couple should remain constant. In fact, the current density–potential behaviour for CH_3 -terminated n -Si(111) interfaces immersed in solutions containing methyl viologen^{2+/1+} (a redox couple whose nernstian potential is unrelated to solution pH) is almost completely invariant to changes in pH (Fig. 9.18). Over a pH range from 1 to 11, the current density–potential responses at CH_3 -terminated n -Si(111) neither change slope nor shift significantly, indicating that k_{ct} has no formal dependence on pH. Accordingly, the data in Fig. 9.18 are strong evidence for the insensitivity of E_{c} and E_{v} at CH_3 -terminated Si electrodes to changes in solution pH. Hence, by introducing $-\text{CH}_3$ groups to the surface of Si, the conduction-band edge at the surface is engineered to a constant energy by manipulation of the pH_{pzc} . If similar surface functional groups possessing vastly different dipole characters, but capable of nominally similar surface coverage, could be used, the energetics of Si ought to be specifiable to any desired energy to maximise k_{ct} according to eq. 9.3.

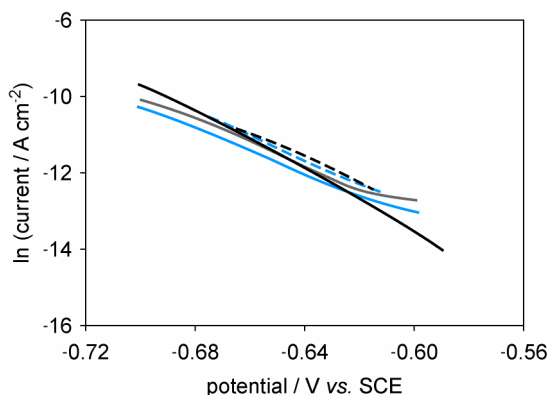


Figure 9.18 Semilogarithmic plots of i vs. U for CH_3 -terminated n -Si electrodes in contact with 10 mM methyl viologen²⁺ at pH = 1.4 (grey continuous line), pH = 3.8 (blue continuous line), pH = 6.8 (blue dashed line), pH = 9.0 (black dashed line), and pH = 11.0 (black). Source: Hamann and Lewis (2006).

9.5 Future directions

Photoelectrochemical systems have advanced greatly over the last half century. A comparison between Table 9.1 and a corresponding table in a review written in 1978 (Nozik, 1978) shows the specific progress in conversion efficiencies. More generally, though, photoelectrochemists have discovered, solved and explained some of the most difficult problems in this area of science during the last fifty years. Researchers have developed a full analytical description of interfacial charge transport at semiconductor/solution interfaces and, in the process, have gained further insight on interfacial charge-transfer processes in general. Researchers have constructed a wide array of photoelectrochemical systems that can sustainably generate either electricity and/or chemical fuels, with some system efficiencies equalling or surpassing analogous solid-state heterojunction devices. Researchers have conceptualised and executed innovative strategies for kinetically protecting thermodynamically unstable materials in water, and have demonstrated deterministic control over the energetics of semiconductor surfaces. Individually, each of these achievements is significant. As a whole, these advances demonstrate the development of this field of science.

To satisfy global energy demands, the field of photoelectrochemistry must continue to develop. The economic and commercial constraints inherent in renewable energies represent further obstacles to overcome. Two distinct, yet equally exciting, new trends in photoelectrochemistry represent such innovative thinking. One approach involves designing photoelectrochemical cells that operate efficiently with low-grade materials by orthogonalising the direction of light absorption and charge collection (Kaye *et al.*, 2005; Maiolo *et al.*, 2007). The other movement is towards designing high-throughput, fast screening procedures to test combinatorially new multi-component semiconductors (Woodhouse *et al.*, 2005). Although both strategies are still in their infancy, each has shown success at the laboratory level. Coupled with the methods outlined in this chapter, there is hope that these and other new strategies will lead to harnessing the power of the Sun cleanly, sustainably and efficiently.

Acknowledgements

We acknowledge the Department of Energy and the National Science Foundation for sustained support of this work in photoelectrochemistry that made the preparation of this review possible.

Table 9.1 Reported Performances of Regenerative Photoelectrochemical Cells

Material	E_g/eV^a	D/I^b	Electrode type ^c	Crystal face	Solvent–supporting electrolyte	Redox couple ^d	$\eta/\%$ ^e	Reference
Metal oxides								
SrTiO ₃	3.2	I	<i>n</i> -SrTiO ₃	NR ^f	H ₂ O–10M KOH	H ₂ O/O ₂	1	Mavroides <i>et al.</i> (1975)
TiO ₂	3.0	I	<i>n</i> -TiO ₂	NR ^f	H ₂ O–10M KOH	H ₂ O/O ₂	0.6	Mavroides <i>et al.</i> (1975)
α -Fe ₂ O ₃	2.2	I	<i>n</i> -Fe ₂ O ₃	polycryst.	H ₂ O–0.7M K ₄ Fe(CN) ₆	Fe(CN) ₆ ^{3-/4-}	0.06	Sanchez <i>et al.</i> (1982)
Group IV compounds								
Si	1.12	I	<i>n</i> -Si	(100)	CH ₃ OH–1M LiClO ₄	Fe ³⁺ /Fe	12.1	Rosenbluth <i>et al.</i> (1984)
			<i>n</i> -Si	(100)	CH ₃ OH–1M LiClO ₄	dmFe ³⁺ /dmFe	14	Gibbons <i>et al.</i> (1984)
			<i>n</i> -Si	polycryst.	CH ₃ OH–1M LiClO ₄	dmFe ³⁺ /dmFe	9.6	Gibbons <i>et al.</i> (1984)
			<i>n</i> -Si	(111)	H ₂ O–8.6M HBr	Br ₂ /Br [–]	9	Yae <i>et al.</i> (2001)
			<i>p</i> -Si(Pt)	(100)	H ₂ O–4M HCl	V ³⁺ /V ²⁺	2.8	Heller (1980)
			<i>p</i> -Si	(100)	CH ₃ CN–1M TEA(BF ₄)	Cc ⁺ /Cc	10	Lieber <i>et al.</i> (1984)
a-Si:H	1.7	D	<i>n</i> -(a-Si:H)	amorphous	CH ₃ OH–1.5M LiClO ₄	Fe ³⁺ /Fe	7.6 (514 nm)	Gronet <i>et al.</i> (1984)
III–V compounds								
InP	1.35	D	<i>p</i> -InP	(111)A	H ₂ O–4M HCl	V ³⁺ /V ²⁺	11.5	Heller (1981)
			<i>p</i> -InP	(111)A	H ₂ O–4M HCl	V ³⁺ /V ²⁺	9.4	Heller (1981)
			<i>p</i> -InP	polycryst.	H ₂ O–3M HCl	Eu ³⁺ /Eu ²⁺	7	Heller (1983)
			<i>p</i> -InP	polycryst.	H ₂ O–1M NaOH	S _n ^{2-/S} ^{2–}	6	Ang and Sammells (1983)
			<i>p</i> -InP	(100)	CH ₃ OH–1M LiClO ₄	dmFe ³⁺ /dmFe	7	Heben <i>et al.</i> (1989)
			<i>p</i> -InP	(100)	AlCl ₃ –butylpyridinium chloride	Fe ³⁺ /Fe	0.4	Thapar <i>et al.</i> (1982)

Material	E_g/eV^a	D/I ^b	Electrode type ^c	Crystal face	Solvent–supporting electrolyte	Redox couple ^d	$\eta/\%^e$	Reference
GaAs	1.43	D	<i>n</i> -GaAs	(111)	H ₂ O–1M KOH	Se _n ²⁻ /Se ²⁻	9–14	Chang <i>et al.</i> (1977)
				(100)	H ₂ O–1M KOH	Se _n ²⁻ /Se ²⁻	12	Parkinson <i>et al.</i> (1979) Noufi and Tench (1980)
			<i>n</i> -GaAs(Os ³⁺)	epitaxial	H ₂ O–1M KOH	Se _n ²⁻ /Se ²⁻	15	Tufts <i>et al.</i> (1987)
			<i>n</i> -GaAs	polycryst.	H ₂ O–1M KOH	Se _n ²⁻ /Se ²⁻	7–8	van Meirhaeghe <i>et al.</i> (1979) Heller <i>et al.</i> (1980)
			<i>n</i> -GaAs	NR ^f	CH ₃ CN– 0.1M N(C ₄ H ₉) ₄ ClO ₄	Fc ⁺ /Fc	14	Kohl and Bard (1979)
			<i>n</i> -GaAs	(111)	AlCl ₃ –butylpyridinium chloride	Fc ⁺ /Fc	1	Singh <i>et al.</i> (1981)
GaAsP	1.77	D	<i>n</i> -GaAs _{0.72} P _{0.28}	epitaxial	H ₂ O–1M KOH	Se _n ²⁻ /Se ²⁻	11	Gronet and Lewis (1984)
			<i>n</i> -GaAs _{0.72} P _{0.28}	epitaxial	CH ₃ OH– 0.1M N(C ₂ H ₅) ₄ BF ₄	Fc ⁺ /Fc	13.2	Gronet and Lewis (1982)
Al _{0.09} Ga _{0.91} As	1.51	D	<i>n</i> -Al _{0.09} GaAs _{0.91}	epitaxial	CH ₃ CN–0.7M LiClO ₄	Fc ⁺ /Fc	9	Casagrande <i>et al.</i> (2000)
II–IV chalcogenides								
CdS	2.42	D	<i>n</i> -CdS	(0001)	H ₂ O–1M KCl	Fe(CN) ₆ ^{3-/4-}	15–18 (488 nm)	Rubin <i>et al.</i> (1984)
			<i>n</i> -CdS	(0001)	H ₂ O–1M cysteamine, 1M Na ₂ SO ₄	RSH/RSSR	15 (501.7 nm)	Natan <i>et al.</i> (1986)
			<i>n</i> -CdS	(0001)	CH ₃ CN–0.1M LiClO ₄	I ₃ ⁻ /I ⁻	9.5 (475 nm)	Nakatani <i>et al.</i> (1978)
CdSe	1.7	D	<i>n</i> -CdSe	(1120)	H ₂ O–0.5M KOH, 0.1 KCN	Fe(CN) ₆ ^{3-/4-}	16.4	Licht and Peramunage (1990)
			<i>n</i> -CdSe	(1120)	H ₂ O–1M NaOH	S _n ²⁻ /S ²⁻	7	Heller <i>et al.</i> (1978)

Material	E_g/eV^a	D/I ^b	Electrode type ^c	Crystal face	Solvent–supporting electrolyte	Redox couple ^d	$\eta/\%$ ^e	Reference
			<i>n</i> -CdSe	NR ^f	CH ₃ OH– 0.1M N(C ₂ H ₅) ₄ BF ₄	Fe(CN) ₆ ^{3-/4-}	6	Noufi <i>et al.</i> (1981)
			<i>n</i> -CdSe	polycryst.	H ₂ O–1M NaOH	S _n ^{2-/S} 2-	7–8	Manassen <i>et al.</i> (1977) Miller <i>et al.</i> (1977) Reichman and Russak (1984)
CdTe	1.56	D	<i>n</i> -CdTe	(111)	H ₂ O–5M NaOH	Se ₂ ^{2-/Se} 2-	9 (633 nm)	Ellis <i>et al.</i> (1977)
				(111)	H ₂ O–5M NaOH	Te ₂ ^{2-/Te} 2-	10 (633 nm)	Ellis <i>et al.</i> (1977)
CdSeTe	1.4	D	<i>n</i> -CdSe _{0.81} Te _{0.19}	polycryst.	H ₂ O–1MKOH	S _n ^{2-/S} 2-	7 (840 nm)	Russak and Crater (1984)
			<i>n</i> -CdSe _{0.65} Te _{0.35}	(1120)	H ₂ O–1.8M KOH, 3M S ₂	S _n ^{2-/S} 2-	12	Licht <i>et al.</i> (1985)
Lamellar chalcogenides								
MoS ₂	1.17	I	<i>n</i> -MoS ₂	basal plane	H ₂ O–2M KI	I ₃ ^{-/I} -	4.1	Kline <i>et al.</i> (1982)
MoSe ₂	1.06	I	<i>n</i> -MoSe ₂	basal plane	H ₂ O–2M KI	I ₃ ^{-/I} -	9	Kline <i>et al.</i> (1982)
MoTe ₂	1	I	<i>n</i> -MoTe ₂	basal plane	H ₂ O–5M KI	I ₃ ^{-/I} -	8 (633 nm)	Abruna and Bard (1982)
WS ₂	1.3	I	<i>n</i> -WS ₂	basal plane	H ₂ O–1M HBr	Br ₂ /Br ⁻	6	Kline <i>et al.</i> (1982)
			<i>p</i> -WS ₂	basal plane	CH ₃ CN– 0.1M [<i>n</i> -Bu ₄ N]ClO ₄	dcFe ^{+/dc} Fe	7 (632.8 nm)	Baglio <i>et al.</i> (1983)
WSe ₂	1.16	I	<i>n</i> -WSe ₂	basal plane	H ₂ O–1M NaI	I ₃ ^{-/I} -	8–14	Kline <i>et al.</i> (1982) Tenne and Wold (1985) Agarwal and Rao (1989)
			<i>n</i> -WSe ₂	basal plane	H ₂ O–1M KCl	Fe(CN) ₆ ^{3-/4-}	4	Agarwal and Rao (1989)
InSe	1.3	D	<i>n</i> -InSe	edge plane	H ₂ O–0.1M H ₂ SO ₄ , 0.2M FeSO ₄	Fe ^{2+/Fe} 3+	5	Tenne <i>et al.</i> (1985)

Material	E_g/eV^a	D/I ^b	Electrode type ^c	Crystal face	Solvent– supporting electrolyte	Redox couple ^d	$\eta/\%$ ^e	Reference
Ternary chalcogenides								
CuInS ₂	1.5	D	<i>n</i> -CuInS ₂	polycryst.	H ₂ O–2M HI, 2.5M CaI ₂	I ₃ [−] /I [−]	9.7	Lewerenz <i>et al.</i> (1986)
CuInSe ₂	1.03	D	<i>n</i> -CuInSe ₂	(112)	H ₂ O–6M KI, 0.1M Cu ²⁺ , 0.01M In ³⁺	I ₃ [−] /I [−]	12	Menezes <i>et al.</i> (1984) Cahen <i>et al.</i> (1986)
			<i>n</i> -CuInSe ₂	polycryst.	H ₂ O–2M KI, 2M HI	I ₃ [−] /I [−]	6–12	Szot and Haneman (1986) Lewerenz <i>et al.</i> (1986) Razzini <i>et al.</i> (1986)
Multijunction electrodes^g								
<i>n</i> - Si/Tl ₂ O ₃				Si(111)	H ₂ O–1M NaOH	Fe(CN) ₆ ^{3−} /Fe(CN) ₆ ^{4−}	11	Switzer (1983)
<i>n</i> - Si/Li ₂ O, MgO/Pt				Si(100)	H ₂ O–6M HBr	Br ₂ /Br [−]	13	Howe and Fleisch (1987)
<i>n</i> - Si/MgO/Pt				Si(100)	H ₂ O–6M HBr	Br ₂ /Br [−]	11	Howe and Fleisch (1987)
<i>n</i> - Si/Al ₂ O ₃ /Pt				Si(100)	H ₂ O–6M HBr	Br ₂ /Br [−]	10	Howe and Fleisch (1987)
<i>n</i> - Si/SiO _x /Pt				Si(100)	H ₂ O–6M HBr	Br ₂ /Br [−]	9	Howe and Fleisch (1987)
<i>n</i> - Si/SiO _x /Pt				Si(100)	H ₂ O–0.1M KCl (pH = 0.3)	I ₃ [−] /I [−]	4	Howe and Fleisch (1987)
<i>n</i> - GaAs/ <i>n</i> - SrTiO ₃				GaAs(100)	H ₂ O–0.1M KOH	IO ^{3−} /I [−]	14	Sun and Campet (1990) Campet <i>et al.</i> (1989)
GaAs/Si				Si(100)	H ₂ O–4M HCl	V ³⁺ /V ²⁺	19.1	Licht <i>et al.</i> (1998)
AlGaAs/Si				Si(100)	H ₂ O–4M HCl	V ³⁺ /V ²⁺	19.2	Licht <i>et al.</i> (1998)
AlGaAs/Si				Si(100)	H ₂ O–1M K ₂ S ₂	S _n ^{2−} /S ^{2−}	19.7	Licht <i>et al.</i> (1998)
AlGaAs/Si				Si(100)	H ₂ O–4M HI	I ₃ [−] /I [−]	19.3	Licht <i>et al.</i> (1998)

^a E_g = bandgap at 298 K; ^b D = direct, I = indirect; ^c The counter electrode is any material that supports sufficiently rapid charge-transfer kinetics for the redox couple. ^d Fc = ferrocene, Cc = cobaltocene, dmFc = 1,1'-dimethylferrocene, dcFc = decamethylferrocene; ^e Efficiency $\eta = 100(\text{IscVoc})/\text{FF}/\text{Pin} \%$; values followed by a wavelength are for monochromatic light; ^f NR = not reported; ^g Named from the innermost to the outermost layer; the crystal face is that of the former.

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CHAPTER 10

PHOTOELECTROCHEMICAL STORAGE CELLS

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And the Lord said let there be light. And there was light, and it was good.

Yet, energy was often needed at night.

Genesis, modified.

10.1 Introduction

Whereas society's needs for electrical power are largely continuous, clouds and darkness dictate that photovoltaic solar cells have an intermittent output. A photo-electrochemical solar cell (PEC) can generate not only electrical but also electrochemical energy, and provide the basis for a photoelectrochemical solar cell with an energy storage component (PECS). Sufficiently energetic insolation incident on semiconductors can drive electrochemical oxidation/reduction and generate chemical, electrical or electrochemical energy. The range of possible applications includes efficient dye-sensitised or direct solar-to-electrical energy conversion, photoetching, photoelectrochemical water splitting, environmental cleanup and solar energy storage cells. This review encompasses topics focusing on photoenergy storage concepts based on photoelectrochemical processes, but includes a necessary comparison with other methods proposed for the conversion and storage of solar energy. Following this introduction, Sections 10.2–10.4 cover comparative solar storage processes, modes of photoelectrochemical storage and optimisation of photoelectrochemical storage. Section 10.5 gives examples of specific types of

photoelectrochemical storage cells. The chapter concludes with a section on a PECS cell with high solar-to-electrical conversion efficiency that works in the light *and* dark, and is based on multiple semiconductor bandgap devices. Licht (2002 and 2006) provides overviews of PECS cells.

The PEC utilises light to carry out a chemical reaction, thereby converting light to chemical energy. This fundamental difference between the PV solid/solid interface and the PEC solid/liquid interface has several ramifications in cell function and application. Energetic constraints imposed by single-bandgap semiconductors have limited the demonstrated values of photoelectrochemical solar-to-electrical energy conversion efficiency to 16%, although multiple-bandgap cells can lead to significantly higher conversion efficiencies (Licht *et al.*, 1998a, b and c). Photoelectrochemical systems enable not only solar-to-electrical energy conversion, but also photoelectrochemical synthesis, photoelectrochemical production of fuels and photoelectrochemical detoxification of pollutants, dealt with in other chapters in this book series. A system exemplifying photoelectrochemical synthesis is water photoelectrolysis to generate hydrogen. An early demonstration of water photoelectrolysis utilised TiO_2 (bandgap 3.0 eV) (Fujishima and Honda, 1972), and was energetically assisted by a cell pH gradient with an external bias provided by a pH gradient in the cell (Nozik, 1975, 1978). Frank and Bard (1977) have tested various semiconductor particles for photoelectrochemical breakdown of inorganics. Gerischer and Heller (1992) have investigated the theoretical consequences of photocatalytic oxidation of organic materials at TiO_2 particles by sunlight in aerated waters, and application to pollutant detoxification is being carried forward by Fujishima and others, as described by Sakai *et al.* (1995), and by Serpone and Emeline in Chapter 5.

10.1.1 Charge separation, injection and storage

In illuminated semiconductor systems, the absorption of photons generates excited electronic states. These excited states have lifetimes of limited duration. Without a mechanism of charge separation, their intrinsic energy would be lost through recombination. Several distinct mechanisms of charge separation have formed the basis of efficient photoelectrochemical systems. At illuminated, macroscopic semiconductor/liquid interfaces, an electric field (the space-charge layer) occurs and is associated with charge/ion redistribution in the interface. On photogeneration of electron-hole pairs, this electric field impedes recombinative processes by oppositely accelerating and separating these charges, resulting in minority-carrier injection into the electrolytic redox couple.

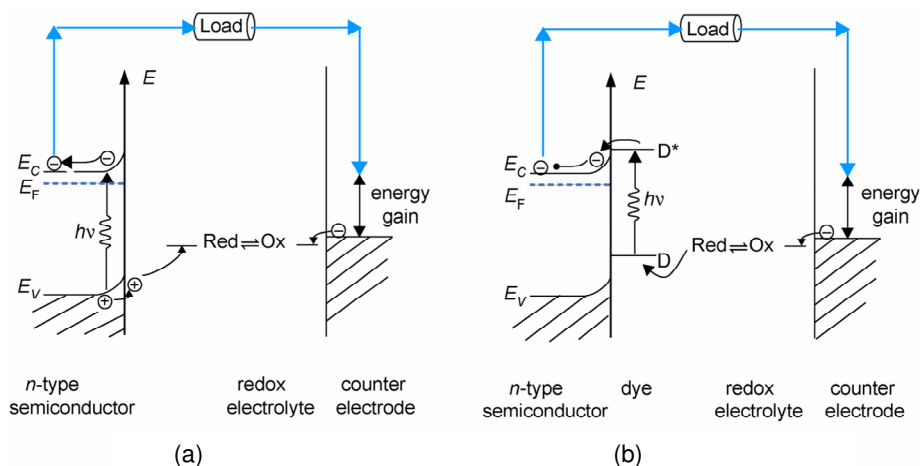


Figure 10.1 Carrier generation under illumination arising at (a) the semiconductor/liquid interface and (b) the semiconductor/dye sensitizer/liquid interface, shown for the case of an *n*-type semiconductor.

This concept of carrier generation, which is illustrated in Fig. 10.1a for an *n*-type PEC, has been the basis of several efficient semiconductor/redox couple PEC cells. Illumination of the electrode surface with light of photon energy greater than the semiconductor bandgap energy promotes electrons into the conduction band, leaving holes in the valence band. An *n*-type semiconductor functions as a photoanode, and band bending in the depletion region drives any electrons that are promoted to the conduction band into the interior of the semiconductor, from which they are extracted by an ohmic contact, while holes in the valence band are driven towards the electrolyte, where they participate in an oxidation reaction. The electrons drive an external load before they reach the counter or storage electrode, where they participate in a reduction process. Illumination of an *n*-type semiconductor on open circuit creates a negative shift in electrode potential, and a consequent negative shift in the Fermi level of the photoanode, reducing the band bending. (Note the negative photoanode shift is according to conventional electrochemical scales, but the same shift would be denoted positive according to the semiconductor physics vacuum scale: see Appendix 1A at the end of Chapter 1.) Under illumination with increasing light intensity, the semiconductor Fermi level shifts progressively towards negative potentials until the band bending approaches zero, which corresponds to the flatband condition. At this point a photoanode exhibits its maximum photovoltage, which is equal to the decrease of the band bending in the dark. The above is appropriate for unpinned Fermi levels (but not pinned ones).

Excitation can also occur in molecules directly adsorbed on the electrode, which can act as mediators at the semiconductor interface. In this dye sensitisation mode, the function of light absorption is separated from that of charge-carrier transport. First the dye is photoexcited, and then photogenerated charge is injected into the semiconductor. This carrier generation mode also can lead to effective charge separation, as illustrated in Fig. 10.1b. O'Regan and Grätzel (1991) provided the first high-efficiency example of such a device in the Grätzel DSSC cell, which has a novel, high-surface area, nanostructured thin-film $n\text{-TiO}_2$ electrode, coated with a trimeric ruthenium complex immersed in an aqueous polyiodide electrolyte. The unusually high surface area of the transparent semiconductor coupled with the well-matched spectral characteristics of the dye lead to a device that harvests a high proportion of insolation. Dye-sensitised solar cells, in particular the Grätzel cell, are treated in Chapter 8.

10.1.2 Photoelectrochemical storage

Photoelectrochemical cells can generate not only electrical but also electrochemical energy. Figure 10.2 shows one example of a PEC that combines solar conversion capabilities with *in situ* electrochemical storage and provides continuous output insensitive to daily variations in illumination. This high-efficiency cell, developed by Licht *et al.* (1987), utilised a $\text{Cd}(\text{Se},\text{Te})/\text{S}_x$ conversion half-cell and a Sn/SnS storage system in a solar cell with a continuous output. Under illumination, the photocurrent drives an external load, as shown in Fig. 10.2a. Simultaneously, part of the photocurrent is used in the direct electrochemical reduction of metal cations in the storage component. In darkness or below a certain light level, the storage compartment spontaneously delivers power by oxidation of Sn to SnS , as shown in Fig. 10.2b.

10.2 Comparative solar energy storage processes

Solar energy can be stored as heat in a number of ways: the heat may be stored physically or chemically and then directly used or released on reversal of a storage process. Limitations of this approach include the low amount of energy stored per unit mass of the storage medium, and the low efficiencies of thermal-to-mechanical and thermal-to-electrical energy conversion. In this section, we discuss some alternative approaches to the storage of solar energy that are capable of higher efficiency or lead to more valuable products than heat.

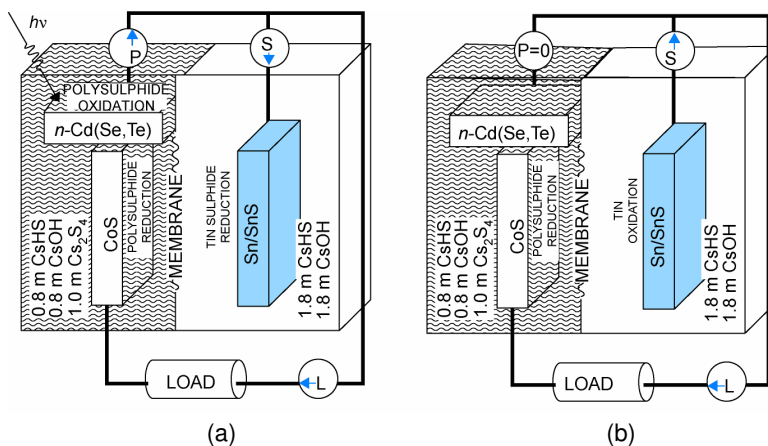


Figure 10.2 Schematic of a photoelectrochemical solar cell combining both solar conversion and storage capabilities. (a) Under illumination; (b) in the dark. From Licht *et al.* (1987).

10.2.1 Thermal conversion and storage

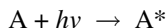
The high temperatures generated by concentrated solar power can be used to drive chemical reactions. The reverse reaction releases the chemically stored energy as thermal energy. Various systems have been investigated, such as the dissociation of sulphur trioxide (De Maria *et al.*, 1985):



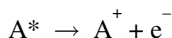
10.2.2 Photochemical storage

In photochemical processes for solar energy storage, photon absorption either creates a molecular excited state or stimulates an interband electronic transition in a semiconductor, which induces a molecular change. Comprehensive reviews, including those by Grätzel (1980), Kalyanasundaram (1982) and Harriman (1986–7), have discussed various aspects of photochemical energy conversion. A photoactivated molecular excited state can drive either i) photodissociation; ii) photoisomerisation; or iii) photoredox reactions. Processes based on semiconductors may involve photovoltaic or photoelectrochemical systems.

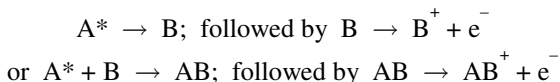
Molecular photoredox processes involve electron transfer from photoinduced excited states:



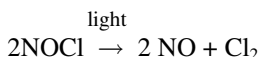
The electron transfer may be either direct:



or it may occur through a variety of indirect processes, as exemplified by either:

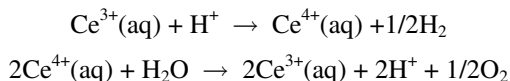


Solar-activated photodissociation processes generally involve cleavage of a simple molecule into several energetic products. Limitations of this approach include the limited absorption of solar energy by the molecule, low quantum yields, rapid back reaction and difficulties separating the product species. Storage by such processes is exemplified by the cell of Marcus *et al.* (1961), based on the reaction



Photoisomerisation reactions, notably the transformation of norbornadiene to quadricyclane (Kutal, 1978), can also be used to store solar energy. Here photon absorption activates molecular rearrangement of organic molecules into strained but metastable isomers. The stored thermal energy can be released by catalytically inducing reversion to the starting components. Despite some attractive features, including high heat storage capacity and good thermal stability, such systems have poor efficiencies. They require molecules to take up high-energy strained conformations, and their threshold wavelengths are generally below 450 nm.

Photochemical redox reactions can generate fuel, including H_2 , CH_4 and CH_3OH . The splitting of water to produce hydrogen has been the focus of particular attention. H_2O is transparent to solar UV or visible radiation, and therefore sensitisation is required to drive the water-splitting process. In the early attempts at the photoredox splitting of water of Heidt and McMillan (1953), the process was sensitised by solution redox species such as $\text{Ce}^{3+/4+}$:



These processes have poor quantum yields. As in photoisomerisation processes, the reactions are generally driven only by short-wavelength radiation, and cannot efficiently convert AM1 solar radiation.

The generation of molecular hydrogen or oxygen from water is a multi-electron process, and optimisation of the photoredox splitting of water requires the presence of one or more catalysts to mediate the complex electron transfers. Figure 10.3 shows a process of this kind, described by Kutal (1983), in which the sacrificial reagent triethanolamine (TEOA) is irreversibly consumed. Concerted multi-electron processes are rare, and photoredox processes usually incorporate one or more intermediate steps involving radicals. These reactive intermediates are susceptible to unfavourable side reactions, resulting in substantial losses in energy conversion efficiency. Kinetically-favoured back reactions further reduce the overall conversion efficiency. The engineering of these complex molecular reorganisations provides a substantial scientific challenge, and they have generally resulted in systems with low conversion efficiencies.

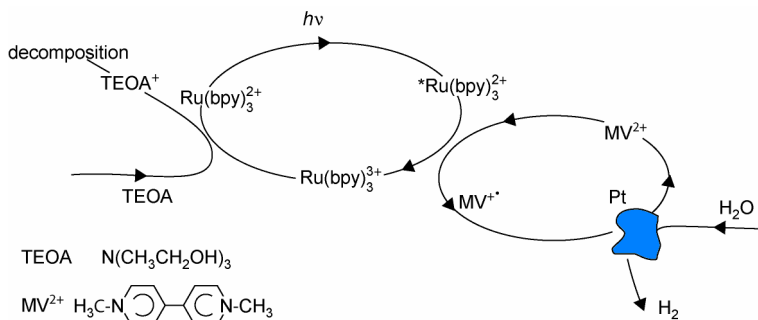


Figure 10.3 Sacrificial system for the photochemical production of hydrogen. From Kutal (1983).

10.2.3 Semiconductor photoredox storage

Semiconductor surfaces have been utilised as sensitisers to drive photochemical conversion and storage of solar energy. In principle, this should lead to a higher level of photon absorption and more effective charge separation. Both phenomena can substantially increase solar photochemical conversion efficiency, but these systems have not yet displayed high efficiencies of fuel generation or long-term stabilities.

The semiconductor SrTiO_3 was demonstrated to split water successfully in a direct photon-driven process by Bolts and Wrighton (1976), albeit at low solar energy conversion efficiencies. The high SrTiO_3 bandgap of 3.2 eV creates sufficiently energetic charge to drive the photoredox process. This excludes the longer wavelength

photons and harnesses only a small fraction of incident solar radiation. To improve the solar response, the bandgap has to be lowered and in a single bandgap system, an optimum efficiency can be expected around 1.4 eV.

Colloids and suspensions of semiconductors have also been utilised for the photoredox splitting of water. The principal advantage of a fine suspension is the large active surface area available. Reaction rates of H_2 and O_2 generation have been enhanced by loading the particles with small deposits of precious metals, as described by Memming (1988), but no practical system has been demonstrated.

In photoelectrochemical water-splitting systems, corrosion of the semiconductor photoelectrodes can pose a significant problem. The earliest combined *p*- and *n*-photoelectrode systems for water splitting include those of Yoneyama *et al.* (1975) and Nozik (1976). Most surface-stabilising redox reactions compete with H_2 and O_2 generation, and must be excluded from these systems. In order to enhance the solar response of wide-bandgap materials, techniques such as dye sensitisation and impurity sensitisation have been employed by Maruska and Ghosh (1978), although with little improvement in water-splitting efficiency. Semiconductor surfaces have been modified to protect low-bandgap materials against photocorrosion, for example by Hodes *et al.* (1983) and Kainthla *et al.* (1986). A self-driven photoelectrochemical cell by Kainthla and Bockris (1988), consisting of Pt-coated *p*-InP and Mn-oxide-coated *n*-GaAs, has been demonstrated to operate at 8.2% maximum efficiency to generate H_2 and O_2 under simulated sunlight. Khaselev and Turner (1998) have also used a two-bandgap photovoltaic cell in a tandem arrangement to split water at 12% efficiency, and Licht *et al.* (2001) have split water at 18.3% efficiency using a cell containing illuminated AlGaAs/Si $\text{RuO}_2/\text{Pt}_{\text{black}}$ to evolve H_2 and O_2 . In the latter system, isolating the RuO_2 oxygen electrode and the Pt_{black} from the semiconductors eliminated the problem of semiconductor photocorrosion.

Subsequently, one of us (Licht, 2003; Licht *et al.*, 2003; Licht, 2005) has developed a quantitative photothermal–electrochemical theory of water splitting which provides a path to experimental solar-to-hydrogen energy conversion efficiencies of over 30%. The photothermal–electrochemical process utilises near-IR and IR insolation, along with the conventional near-UV and visible components of the solar spectrum. The significant potential energy carried in these additional (thermal) solar photons had not been available to other photoelectrochemical processes, as these photons have insufficient energy to excite the semiconductor sensitisers. The redox potential, and energy, required to split water decreases rapidly with increasing temperature and pressure. This substantially improves the solar-to-hydrogen fuel energy conversion efficiency. As shown in Fig. 10.4, the photothermal–electrochemical process is a hybrid system in which solar thermal photons are used to heat

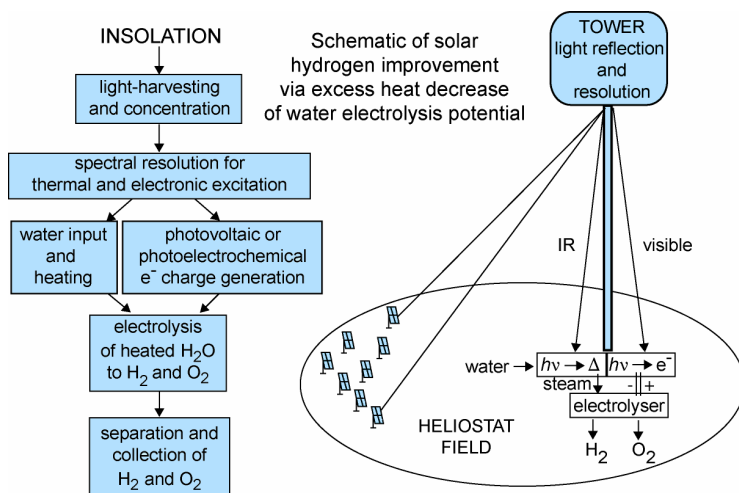


Figure 10.4 Schematic of the photothermal–electrochemical solar splitting of water to generate hydrogen. From Licht (2003).

water and solar visible photons concurrently drive electrolysis of the heated water. Thermodynamic details of the decrease in water's electrochemical potential and the theory of semiconductor band-edge restricted photothermal–electrochemical water splitting are presented in Licht (2003). Experimental details of an example of tuning the water-splitting photopotential to semiconductor energetics are given in a related study (Licht *et al.*, 2003). This study showed that a single PV cell of a relatively small band-gap semiconductor such as silicon can drive ‘temperature-tuned’ water splitting. It also describes using several such PV cells in series to drive a more efficient solar-to-hydrogen fuel conversion process; this can be more efficient than the PV process alone (the silicon photovoltaic cells utilised had a photoconversion efficiency of 26.3% at 50 Suns), when infrared insolation, not needed to drive photoconversion, is used to heat water.

We have not found examples of in the literature of efficient PECS photoredox processes at semiconductor electrodes that generate fuels or products other than hydrogen, such as methanol and ammonia. As another example, the photoelectrolysis of HI into H₂ and I₃[−] at *p*-InP electrodes was described by Memming (1988). These H₂ and I₃[−] photogenerated products are prime candidates for fuelling a fuel cell. Analogous advanced systems, in which the photoelectrochemically-generated fuels have been successfully recombined to generate electrical energy, such as in a hydrogen/bromine fuel cell, are discussed in Section 10.5.4.

10.3 Modes of photoelectrochemical storage

Conversion of a regenerative PEC to a PECS can incorporate several increasingly sophisticated solar energy conversion and storage configurations, which we shall discuss in this section.

10.3.1 Two-electrode configurations

A variety of two-electrode configurations have been investigated as PECS systems; Table 10.1 show and Fig. 10.5 show the important cell types. In all cases, exposure to light drives separate redox couples, and a current through the external load. There is a net chemical change in the system, with an overall increase in free energy. When illumination ceases, the generated chemical change drives a spontaneous discharge reaction and current in the opposite direction through an external load.

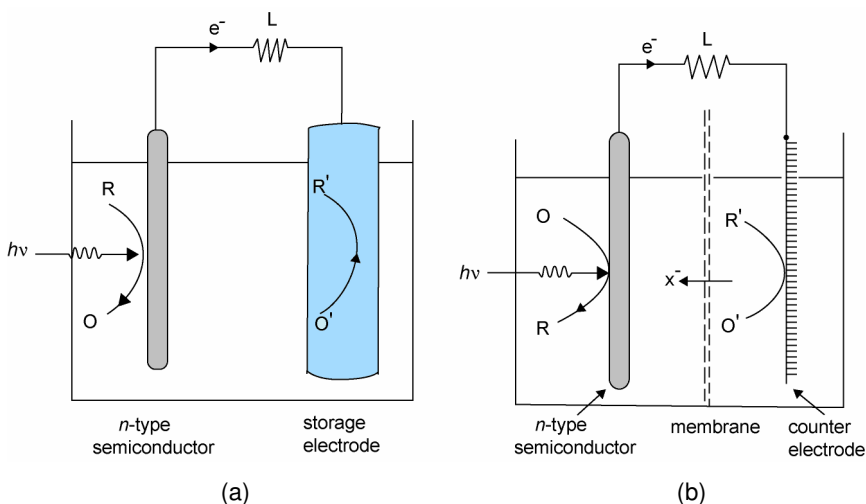


Figure 10.5 Schematic diagram of two-electrode storage cells with (a) an insoluble redox storage couple O' , R' ; (b) a soluble redox storage couple O' , R' . L = load, X^- = counter ion. In each case, the light-driven and dark reactions are:

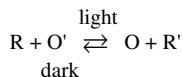


Table 10.1 Some important two-electrode photoelectrochemical conversion and storage configurations

Scheme	Electrode 1	Electrolyte(s)		Electrode 2
I	SPE	Redox A	Redox B	CE
II	SPE	Redox A–membrane–Redox B		CE
III	SPE	Redox A		RedoxB _{CE} –CE
IV	SPE–Redox _{SPE}	Redox B		CE
V	SPE	Redox A–membrane–Redox B		SPE

SPE = semiconductor photoelectrode, CE = counter electrode. At the electrode|electrolyte interface, redox couples A and B are either in solution ($| \text{Redox} |$), or confined to the counter electrode ($| \text{Redox}_{\text{CE}} - \text{CE} |$) or the semiconductor photoelectrode ($\text{SPE} - \text{Redox}_{\text{SPE}} |$).

Unlike the regenerative PEC system shown in Fig. 10.1, in which the electrolyte is continuously regenerated, here there is a net chemical change in a system. The open-circuit voltage V_{oc} depends on the state of charge, and chemical changes taking place in the system during illumination are reversed on discharge in the dark. As in a secondary battery, the system gradually returns to its original chemical state as the system discharges in the dark.

Each of the cells shown in Fig. 10.5 has some disadvantages. For both bound (Fig. 10.5a) and soluble redox couples (Fig. 10.5b), the redox species may chemically react with, and impair, the active materials of the photoelectrode. Furthermore, the photoelectrode is often kinetically unsuited to perform as a counter electrode during the discharge process. In the absence of illumination, the photoelectrode, in this case a photoanode, assumes the role of a counter electrode by supporting a reduction process. For the photoanode to perform efficiently during illumination (charging), this very same reduction process should be inhibited, to minimise photooxidation back reaction losses. The same photoelectrode cannot efficiently fulfill the dual role of being kinetically sluggish to reduction during illumination and being kinetically facile to the same reduction during dark discharge.

As Manassen *et al.* (1981) pointed out, the configurations represented in Fig. 10.5 have another disadvantage, namely the disparity between the small surface area desired to minimise the dark current in the storage electrode or half-cell, since this opposes and reduces the photocurrent, and the large surface area necessary to minimise storage polarisation losses and maximise storage capacity.

10.3.2 Three-electrode configurations

Several of the above-mentioned disadvantages of two-electrode configurations can be overcome by using a three-electrode storage cell configuration, as shown in Fig. 10.6. Here the photoelectrode P operated only when the cell is illuminated, and does not have to double as the counter electrode A, which operates only during discharge in the dark. The switches E and F are generally alternated during charge and discharge. During charging, switch E is closed while switch F is open, and the storage electrode S is charged. During discharge E is open while F is closed. The chemical changes that took place at S during the storage phase are reversed, and a current flow is maintained from the storage electrode to the third (counter) electrode A, which is in the first compartment. To minimise polarisation losses during discharge, this third electrode should be kinetically fast for the redox couple O, R.

A further improvement would be to have both switches closed all the time. In this case electric current flows from the photoelectrode to both the counter and the storage electrodes. The system should be energetically tuned so that a significant fraction of the converted energy flows to the storage electrode under normal sunlight. In the dark or under diminished insolation, the storage electrode begins to discharge, driving continued current through the load. A proper balance should be maintained between the free energy change ΔG of the solar energy conversion process to provide sufficient energy to drive the cell emf needed for the storage process. There may be residual

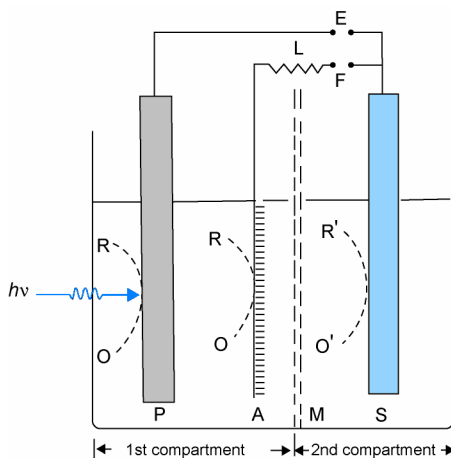


Figure 10.6 Schematic diagram of a storage system with a third electrode (counter electrode) in the photoelectrode compartment. P = Photoelectrode, A = Counter electrode, M = Membrane, S = Storage Electrode, E, F = Electrical switches, L = Load.

electric current flow through the photoelectrode during cell discharge in the dark, as the photoelectrode is sluggish, but not entirely passive, to a reduction process. This can be corrected by inserting a diode between the photoelectrode and the outer circuit.

10.4 Optimisation of photoelectrochemical storage

The power obtained from a cell or battery is the product of voltage and current, and consideration of the photocurrent is as important as the photovoltage. If the band bending in the photoelectrode remains sufficiently large, the minority-carrier redox reaction that is essential to maintain the photocurrent can compete effectively with the recombination of photogenerated electron-hole pairs in the semiconductor, which represent a loss of absorbed photoenergy. Therefore an objective is to maintain sufficient band bending to give good quantum efficiency and at the same time a significant photovoltage, resulting in high fill factors. Illumination of the photoelectrode always reduces its band bending. In principle, one way to maintain sufficient band bending under illumination is to make the band bending in the dark at equilibrium very high, by choosing a redox couple O, R of very high redox potential for a photoanode, and very low potential for a photocathode. However, this may make the photoprocess so endergonic as to be slow. Improvements relating to stability and conversion efficiency are of paramount importance. A brief discussion of these aspects is included in this section.

10.4.1 *Improvement of the photoresponse of a photoelectrode*

To improve the solar response of a photoelectrode, a proper match between the solar spectrum and the bandgap of the semiconductor should be maintained. When a single-bandgap semiconductor is used, a bandgap of ~ 1.4 eV is the most desirable from the standpoint of optimum solar conversion efficiency. An important criterion is that the minority carrier that is driven towards the semiconductor/ electrolyte interface should not participate in a photocorrosion reaction, because this would be detrimental to the long-term stability of the photoelectrode. Photocorrosion can arise from either kinetic or thermodynamic causes, or a mixture of both. From a thermodynamic perspective, a photoanode is susceptible to corrosion if the Fermi level for holes is at a positive potential with respect to the semiconductor corrosion potential (Bard and Wrighton, 1977; Gerischer, 1977). The corrosion can be prevented, or at least

inhibited, by choosing a redox couple of more negative redox potential than that of the corrosion process (Hodes *et al.*, 1976; Heller *et al.*, 1978). The kinetic approach has been to allow another desired redox process to occur at a much faster rate than the photocorrosion reaction (Bolts *et al.*, 1979). Other methods used to minimise photocorrosion include coating the photoelectrode surface with layers such as Se (Frese, 1982), ITO (Hodes *et al.*, 1983) or protective conductive polymer films (Fan, *et al.*, 1981), or using alternate low-bandgap semiconductors (Sharon, 1988) such as CdTe or CdSe rather than CdS (Cahen *et al.*, 1980; Hodes, 1983). Etching of photoelectrode surfaces has also been recognised and widely used as an important treatment to achieve high conversion efficiency (Heller *et al.*, 1977). The efficacy of this is mostly attributed to removal of surface states that may act as trapping centres for photogenerated carriers. A related procedure called photoetching (Tenne and Hodes, 1980), initially developed for CdSe, improves the photoelectrode performance and preferentially removes the surface defects acting as recombination centres.

In addition to a variety of etching procedures, several other surface treatments have been used to improve photoelectrode performance. Examples include a Ga^{3+} ion dip for CdSe (Tomkiewicz *et al.*, 1982), a ZnCl_2 dip for thin-film CdSe (Hodes *et al.*, 1980; Reichman and Russak, 1982), and the deposition of Ru on GaAs (Parkinson, *et al.*, 1979) and on InP (Heller, 1982), and Cu on CdSe (Flaisher *et al.*, 1984). Reasons advanced for the effectiveness of these treatments range from a suppression of dark current to electrocatalysis by surface-deposited metal atoms.

10.4.2 Effect of the electrolyte

The solution-phase chemistry of the electrolyte is an important feature of the cell that can dramatically influence photoeffects. The redox potential of the photoelectrode couple determines equilibrium band bending. As noted above, a photoanode system allied with a more positive potential redox couple exhibits greater band bending (assuming no shift in band edges—this assumption is often valid for redox species that do not specifically interact with the semiconductor surface), which in turn leads to a higher photovoltage and more efficient carrier separation under normal experimental conditions.

Semiconductor photoeffects in a complex redox electrolyte are greatly affected by such solution properties as solution redox level and stability, interfacial kinetics (adsorption), conductivity, viscosity, ionic activity, and transparency within a crucial wavelength region. Suitable redox electrolytes are known to inhibit unfavourable phenomena such as surface recombination and trapping (McEvoy *et al.*, 1985). In

addition, a solution redox couple may have a favourable influence on the PEC system by improving the charge-transfer kinetics, leading to improved stability of the photoelectrode (Reichman and Russak, 1984). Moreover, appropriate additives incorporated in redox electrolytes can enhance the performance of PEC systems. For example, addition of small concentrations of Se to polysulphide electrolytes improves the stability of the CdSe (single crystal)/polysulphide system (Heller *et al.*, 1978). In this case, Se improves performance by reducing S/Se exchange in the surface of the photoelectrode and by increasing the dissolution of the photooxidised product S, which is the rate-determining step in the oxidation of sulphide at the anode. Addition of Cu^{2+} to the I^-/I_3^- electrolyte is known to improve the stability of the CuInX_2 photoelectrode considerably (Cohen and Chen, 1984) and tungsten and molybdenum dichalcogenide photoelectrochemistry in the same electrolyte can be substantially improved by addition of Ag^+ or other metal cations, and by shift of the I^-/I_3^- redox potential (Licht *et al.*, 1995a and b).

For the CdSe/polysulphide system, solution activity and conductivity, efficiency (fill factor) of the photoanode, charge-transfer kinetics at the interface and the stability of the photoelectrode all exhibit improvements in the sequence $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$ for the alkali metal cation of the polysulphide electrolyte. This trend is explained in terms of the secondary cation effect on electrochemical anion oxidation in concentrated aqueous polysulphide electrolytes (Licht *et al.*, 1985 and 1986a-c). In the case of the Cd(Se,Te)/polysulphide system, efficiency of light energy conversion is improved by using a polysulphide electrolyte without added hydroxide, because of the combined effect of increasing the solution transparency, relative increase of S_4^{2-} and decrease of S_3^{2-} in solution. For the same photoelectrode/electrolyte system, an optimum photoeffect was observed for a solution containing a sulphur:sulphide ratio of 1.5 to 2.1 with 1 to 2 molal potassium sulphide concentrations, owing to the combined effect of optimised solution viscosity, transparency, activity and shift in solution redox level (Licht, 1995). Stability of the polysulphide redox electrolyte, which is another parameter that determines the long-term performance of a PEC cell, increases with sulphur and alkali metal sulphide concentration and decreases with either increasing OH^- concentration or at a high ratio of added sulphur to alkali metal sulphide (Licht *et al.*, 1985 and 1986a, b and c; Licht, 1987). As shown in Fig. 10.7, the combined polysulphide electrolyte optimisation substantially enhances conversion efficiency.

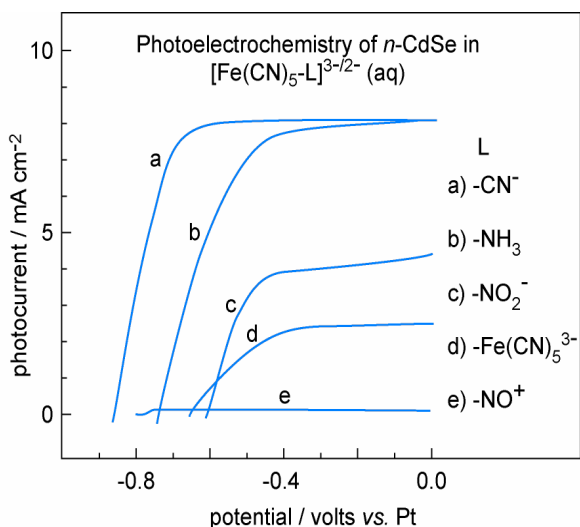


Figure 10.7 Potentiostatic photocurrent-voltage characteristics for an illuminated *n*-CdSe single crystal immersed in electrolytes containing ferrocyanates with replacement of a single cyano ligand by a variety of different ligands. Details of each electrolyte are given in Licht (1995).

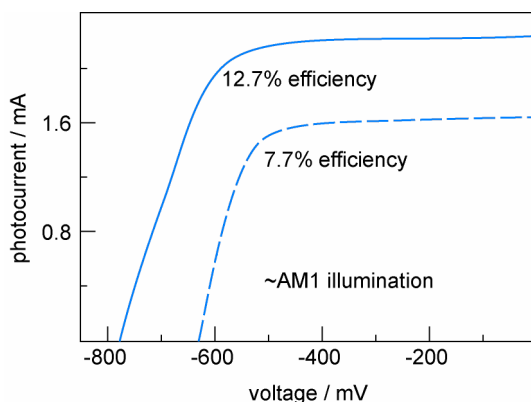


Figure 10.8 Potentiostatic photocurrent-voltage characteristics for an illuminated *n*-CdSe_{0.65}Te_{0.35} single crystal immersed in either of two types of aqueous polysulphide electrolyte. The top curve is for 1.8 M CS₂S and 3 M sulphur; bottom curve is for 1 M NaOH, 1 M Na₂S, 1 M sulphur. The photocurrent-voltage curves were obtained outdoors in sunny conditions and solar-to-electrical conversion efficiencies are indicated.

Chemical composition of the electrolyte is a particularly important parameter in PEC systems based on complex electrolytes such as polysulphide or ferro/ferricyanide. In the latter redox couple, as shown in Fig. 10.8, replacement of one of the hexacyano ligands strongly changes the photoelectrochemical response of illuminated *n*-CdSe due to a combination of electrochemical and spectroscopic effects (Licht, 1995), and addition of the KCN to the electrolyte can increase *n*-CdSe and *n*-CdTe photovoltages by 200 mV (Licht and Peramunage, 1990).

10.4.3 Effect of the counter electrode

In a photoanode system, the occurrence of sluggish counter electrode kinetics for the cathodic process will cause significant polarisation losses and diminish the photovoltage, even at moderate current densities. Minimisation of these kinetic limitations necessitates a counter electrode with good catalytic properties. For example, as shown by Hodes *et al.* (1980a, 1980b), CoS on stainless steel or brass electrodes (which are sulphided in the electrolyte) exhibits electrocatalytic properties towards polysulphide reduction and overpotentials as low as $1 \text{ mV cm}^2 \text{ mA}^{-1}$ have been realised. The particular redox electrolyte used may also have a bearing on the extent of counter electrode polarisation (Reichman and Russak, 1982; Licht *et al.*, 1985).

In PEC systems, a compromise must be maintained to simultaneously optimise the photoelectrode efficiency, stability and electrolytic properties of the electrolyte. Practical PEC systems often require large working and counter electrodes, and their geometric configuration within the PEC system will affect mass transport and cell current. In some cases, advantageous use has been made of selective sluggish counter electrode kinetics towards certain cathodic processes. For example, carbon is a poor cathode for H_2 evolution compared with Pt, and the direct hydrogenation of anthraquinone at a PEC cathode has been avoided by using a carbon anode (Keita and Nadjo, 1984). In this case, such hydrogenation is an undesirable side reaction.

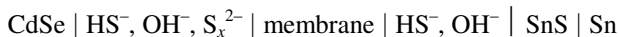
10.4.4 Combined optimisation of storage and photoconversion

An efficient photoelectrochemical conversion and storage system requires not only efficient performance of the separate cell components, but also system compatibility. In the combined photoelectrochemical storage system, simultaneous parameters to be optimised include:

- Minimisation of light losses reaching the photoelectrode.
- Photocurrent quantum efficiency.
- Band bending.
- Close potential match between the photopotential and the required storage charging potential.
- High current and energy efficiency of the redox storage process.
- High energy capacity of the redox storage couple.
- Reversibility (large number of charge/discharge cycles of the redox storage couple).
- Stability of the photoelectrode.
- Stability of the electrolyte.
- Stability of the counter electrode.
- Economy and cost effectiveness.
- Low toxicity and utilisation of environmentally benign materials.

Photoelectrochemical solar cells, including PECS cells containing storage, implicitly contain an electrolytic medium. In the majority of laboratory PEC configurations, incident light travels through the electrolytic medium prior to illuminating the photoelectrode. The resultant light absorption by the electrolyte is a significant loss, which is avoided by use of a back-cell configuration. For example, the substantial absorptivity of dissolved polyselenide species has been avoided in *n*-GaAs photoelectrochemistry through use of the back-wall cell configuration shown in Fig. 10.9 (Forouzan and Licht, 1995; Licht and Forouzan, 1995).

The photoelectrochemical system shown in Fig. 10.6 is a combination of a photoelectrode, electrolyte, membrane, storage and counter electrode. As an example of the challenges that may arise in a combined photoconversion and storage system, consider the following *n*-CdSe/polysulphide/tin sulphide version of Fig. 10.2:



Under illumination, the following simultaneous photoelectrode, counter electrode and storage reactions and equilibria occur in the cell:



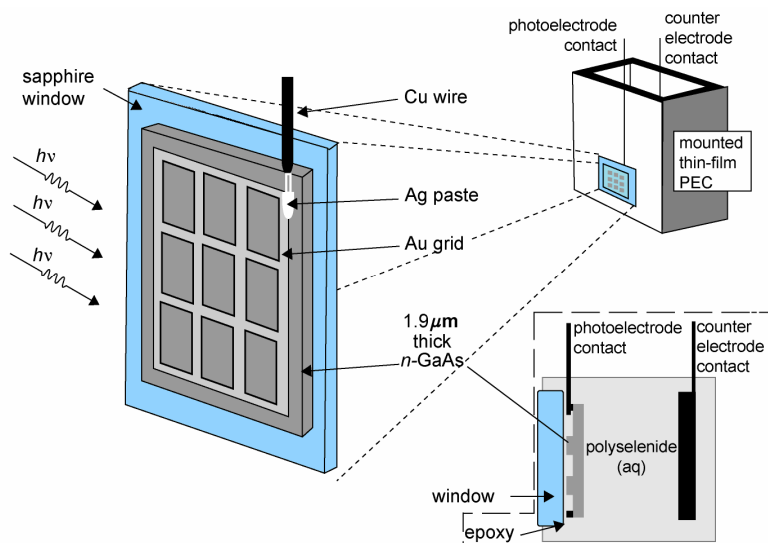


Figure 10.9 A back-wall n -GaAs/aqueous polyselenide photoelectrochemical cell. From Licht and Farouzan (1995).

Unlike the case of the regenerative PEC system, sulphur formed at the photoanode (and dissolved as polysulphide species, $S_{(x+1)}^{2-}$) is here not balanced by the reduction reaction at the counter electrode, because of the simultaneous reduction process taking place at the storage electrode. As a result, sulphur is accumulated in the photoelectrode compartment, and is removed only in the subsequent discharge process. This dynamic variation in electrolyte composition may have a profound influence on the stability of the photoelectrode and electrolyte, and on cell potential. To minimise these effects, either excess polysulphide must be included in the photocompartment, or a limit must be set to the maximum depth of cell charge and discharge.

Another important consideration is the energy compatibility between the photoconversion and storage processes, a requirement also referred to as voltage optimisation. Figure 10.10 shows the combined I - V characteristics for an ideal photoelectrode and current-voltage curves for two possible redox processes: process-A and process-B. V_{ph} is the maximum photovoltage that can be generated, and I_{sc} is the short-circuit photocurrent corresponding to maximum band bending. Consider the electrochemical process represented by curve B in Fig. 10.10. This process is located outside the region of photopotentials generated by the photoelectrode, and therefore does not represent a storage system that can be driven by this single photoelectrode. In such a case, a series combination of more than one photoelectrode would be

necessary. For a redox process to be a potential candidate for a redox storage system, the storage and photodriven current–voltage curves should intersect. Whereas V_{ph} and I_{sc} correspond to zero power, the point P_{mp} shown in Fig. 10.10 corresponds to the maximum-power point. Solar energy conversion is accomplished at its maximum efficiency only when the photoelectrode operates at a potential in the vicinity of P_{mp} .

By adjusting the electrical load L shown in Fig. 10.6, the system can be constrained to operate near its maximum power efficiency. In this case, if the counter electrode is not polarised, the potential difference between photoelectrode and the counter electrode will be close to V_{mp} . If one chooses a facile redox process for the storage electrode, such as process A in Fig. 10.10 with its sharply rising I – V curve, and if, as shown, its U_{redox} is in the vicinity of V_{mp} , then the electrode potential during charge and discharge of the storage process will remain near V_{mp} . As a result the cell output voltage will be almost invariant and current will be maintained through the load L regardless of insolation intensity. This situation represents an ideal match between solar energy conversion and storage processes within a PECS. Non-ideality occurs with poor voltage matching, or kinetic limitations and polarisation losses associated with the counter, storage or photoelectrodes.

Ideally the membrane that separates the two cell compartments, shown in Fig. 10.6, must be permeable only to ions that will transport charge but will not

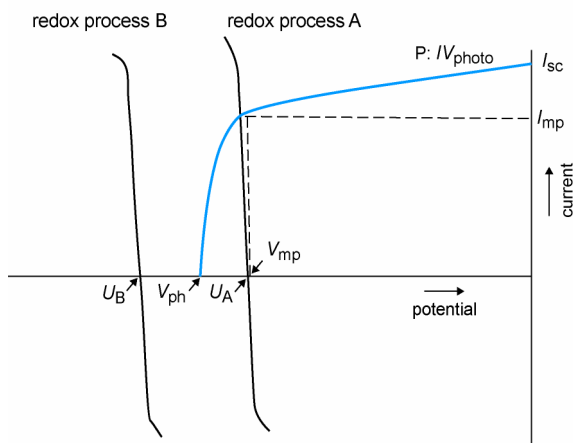


Figure 10.10 Current–voltage curves for electrochemical storage processes, A or B. U_A and U_B are the redox potentials for the respective storage processes. Process A may be charged by the photodriven current–voltage curve P , whereas process B may not. In the photodriven I – V curve P , V_{mp} is the voltage corresponding to the point of maximum power, P_{mp} , and I_{sc} and V_{ph} are the short-circuit current and open-circuit photopotential respectively.

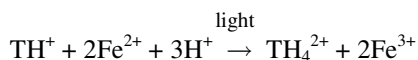
chemically react or otherwise impair any electrode. Unfortunately, the selectivity of membrane permeability is generally less than ideal: most membranes allow other ions and water to permeate to a varying degree (Bratin and Tomkiewicz, 1982; Licht and Manassen, 1987). Gross mixing of active materials across the membrane causes them to combine chemically and in the process lose energy. Favourable qualities a membrane should exhibit are low permeability towards chemically reactive ions, low resistivity, mechanical integrity and cost effectiveness.

10.5 Examples of photoelectrochemical storage cells

Several photoelectrochemical storage cells (PECSs) have been suggested, designed and tested for their performance, under sunlight or artificial illumination. Though none of these has as yet found its way into a commercial-scale development, they are of significant scientific interest and form a solid basis for further development of future systems. This section provides a brief summary of some of these cells, with emphasis on their performance. All of them can be separated into two main categories with respect to the type of storage—solution-phase storage or solid-phase storage.

10.5.1 PECS cells with solution-phase storage

Earlier light-to-electricity conversion cells were often based on the photogalvanic effect, whereby light was absorbed in a dye in solution or adsorbed on an electrode surface. The iron–thionine cell of Murphy (1978) provides an example of a photogalvanic device with storage. The forward reaction is:



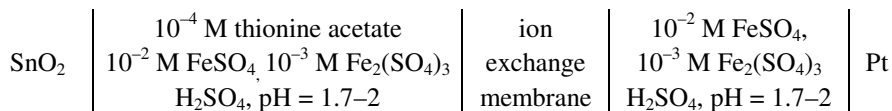
where TH^+ is thionine acetate. The back reaction between leucothionine (TH_4^{2+}) and Fe^{3+} is slow. Leucothionine is selectively oxidised at the SnO_2 electrode



while Fe^{3+} is reduced at a Pt electrode in a second compartment. The concentration ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ is thereby increased in the first compartment and decreased in the second compartment, which produces a difference in redox potential. The system returns to its original uncharged state on discharging in the dark. However, a decadic

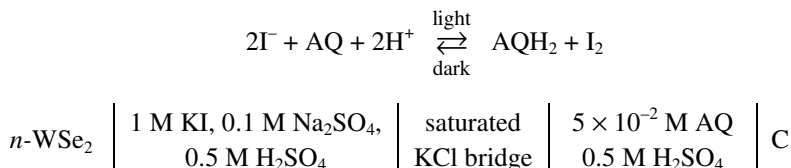
change of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ concentration ratio generates a potential difference of only 60 mV, so the cell does not generate a significant emf, and its power density is low.

Murphy's cell has the configuration:



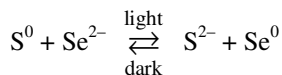
Cell characteristics: polycrystalline SnO_2 photoelectrode, Pt counter electrode, U_{redox} of $\text{Fe}^{3+}/\text{Fe}^{2+} = 0.77 \text{ V vs. SHE}$, illumination $40\text{--}50 \text{ mW cm}^{-2}$ by a tungsten lamp, initial current during discharge = $9.1 \mu\text{A}$, initial voltage = 10.9 mV.

The other cells described in this section have a light-absorbing semiconductor as photoelectrode (mostly *n*-type semiconductors, but also some with *p*-type) and a membrane or salt bridge separating the two electrolytes. Some of the most efficient cells have been based on single crystals of *n*- MoSe_2 or WSe_2 . One example used an anthraquinone (AQ) redox couple, together with an *n*- WSe_2 photoanode in iodine electrolyte (Keita and Nadjao, 1984). A carbon electrode was selected as the counter electrode because of its high overpotential for hydrogen evolution (any H_2 evolution would have resulted in the direct hydrogenation of AQ and associated side reactions). The cell underwent several deep charge and discharge cycles with reproducible performance. The storage reaction and cell form are:



Cell characteristics: single-crystal photoelectrode, carbon counter electrode used during charging, Pt electrode during discharging. U_{redox} of $\text{I}^{3-}/\text{I}^- = 0.534 \text{ V vs. SHE}$, illumination 150 mW cm^{-2} He-Ne laser (632.8 nm). Cell configuration is similar to that in Fig. 10.5. Conversion efficiency = 9%, discharge across a 10 ohm load produces a current of 1 mA cm^{-2} , open-circuit voltage 200 mV.

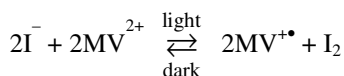
While this cell utilised a salt bridge to separate the two electrolytes, many systems used a membrane instead. Ang and Sammells (1980) provided an example of a membrane cell with a polycrystalline *n*- CdSe photoelectrode that drove a polysulphide/polyselenide storage couple. The cell had reasonable conversion efficiency (4%), but low output power density. The storage reaction and cell configuration are:



n-CdSe | 1 M in Na₂S, S, NaOH | Nafion 315 | 1 M in M Na₂Se, Se, NaOH | Pt

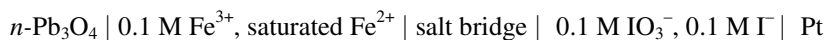
Cell characteristics: polycrystalline photoelectrode, Pt counter electrodes, cell configuration as in Fig. 10.6, U_{redox} of polysulphide electrolyte = -700 mV vs. SCE, U_{redox} of $\text{Se}_2^{2-}/\text{Se}^{2-} = -800$ mV vs. SCE, illumination 100 mW cm^{-2} xenon lamp. Conversion efficiency 4%, $\eta_{\text{fill}} = 0.45$, photovoltage = -400 mV. Charged cell has an open-circuit voltage of 60 mV and initial current through a 100 ohm load across the Pt electrode of 0.5 mA.

Fan *et al.* (1980) provided an example of a PECS cell which uses both *n*- and *p*-type WSe₂ electrodes. Utilising dual (*n*- and *p*-type) photoelectrodes expands the potential regime one can access for the redox storage couple. The theoretical bandgap of WSe₂ provides a near ideal single-bandgap match for the solar spectrum, but this cell has some disadvantages. These include the low solubility of the storage redox couple employed, $\text{MV}^{2+}/\text{MV}^{+\bullet}$, and the possibility of undesirable side reactions of the radical ion $\text{MV}^{+\bullet}$. The storage reaction and cell configuration are:



Other cells using solution-phase storage are listed below with their inventors, structures and some performance parameters.

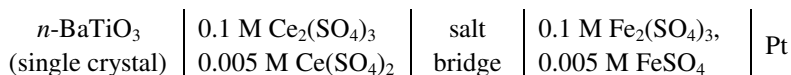
Sharon *et al.* (1984)



Cell characteristics: polycrystalline photoelectrode, Pt counter electrodes, three-electrode configuration as in Fig. 10.6, but with a salt bridge. U_{redox} of $\text{Fe}^{3+}/\text{Fe}^{2+} = 0.77$ V vs. SHE, U_{redox} of $\text{IO}_3^-/\text{I}^- = -0.26$ V vs. SHE, illumination 60 mW cm^{-2} quartz halogen lamp, conversion efficiency = 0.09%, $\eta_{\text{fill}} = 0.38$, photopotential = 172 mV, $V_{\text{mp}} = 172$ mV, charge efficiency of the battery = 74%, potential difference between Pt electrodes before charging = 720 mV, after charging = 840 mV.

Sharon and Singha (1982)

This cell used a wide-gap semiconductor BaTiO₃ ($E_g = 3.3$ eV). This is capable of absorbing only near UV radiation, which comprises less than 5% of available solar energy, and this limits the practical use of the cell for solar energy conversion.



Cell characteristics: Pt counter electrode, three-electrode configuration as in Fig. 10.6, U_{redox} of $\text{Ce}^{4+}/\text{Ce}^{3+} = 1.45$ V vs. SHE, U_{redox} of $\text{Fe}^{3+}/\text{Fe}^{2+} = 0.77$ V vs. SHE, illumination sunlight, conversion efficiency = 0.01%, $\eta_{\text{fill}} = 0.26$, photopotential = 730 mV, $V_{\text{mp}} = 0.33$ V, charge efficiency 15%, potential across two Pt terminals of the charged cell = 0.60 V, short-circuit current = 0.12 mA.

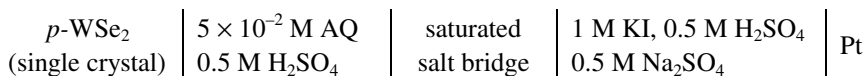
Ang and Sammells (1980)



Cell characteristics: single-crystal photoelectrode, Pt counter electrode, cell configuration as in Fig. 10.6. U_{redox} of $\text{Br}/\text{Br}^- = 1.087$ V vs. SHE, U_{redox} of $\text{I}_3^-/\text{I}^- = 0.534$ V vs. SHE. Illumination 200 mW cm⁻² Xe lamp, conversion efficiency = 6.2%, potential across two Pt terminals of the charged cell = 0.49 V, short-circuit current = 0.5 mA.

Keita and Nadjao (1984)

This study utilised a *p*-WSe₂ photocathode, rather than *n*-WSe₂. During the cell discharge, oxidation of AQH₂ at the surface of *p*-WSe₂ indicates that the electrode has the dual role of acting as a cathode during the charging, and an anode during the discharge. As previously discussed, this limits the activity, and low current densities were observed.

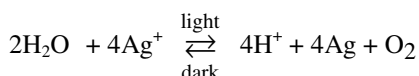


10.5.2 PECS cells including a solid-phase storage couple

The use of a solid-phase storage couple may in principle increase the cell's storage capacity. Having at least one component in insoluble form may add compactness into

the cell configuration, although conductivity of the insoluble active component may introduce significant polarisation losses associated with the storage electrode.

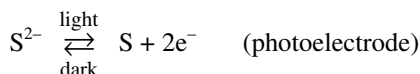
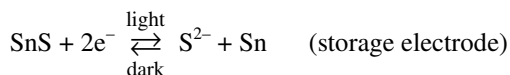
Many of the earlier studies used TiO_2 as photoanode because of the stability of this semiconductor. While the high bandgap of TiO_2 precluded an efficient cell based on solar radiation, it was useful for these early studies into integrated storage cells. These cells were usually based on reduction of Ag or Cu ions to the metal, which subsequently reoxidised on discharge. An example is one of the cells described by Hada *et al.* (1981), in which the storage reaction and cell configuration are:



TiO_2 | 1 M HNO_3 , 1 M KNO_3 | anion-specific membrane | 1 M AgNO_3 , 1 M KNO_3 | Ag

Cell characteristics: polycrystalline photoelectrode, Pt counter electrodes, cell configuration is similar to Fig. 10.6, U_{redox} of O_2 , $\text{H}^+/\text{H}_2\text{O}$ couple = 1.23 V vs. SHE at pH = 0, U_{redox} of Ag/Ag^+ = 0.80 V vs. SHE, illumination 500 W Hg lamp, conversion efficiency = 1%, photopotential = 0.28 V vs. SHE, open-circuit voltage of the charged cell = 0.28 V, short-circuit current = 0.3 mA cm^{-2} .

Various other metal/metal ion storage systems with lower bandgap (and therefore potentially much more efficient) photoelectrodes have been studied. An example of an efficient cell with an output that is highly invariant despite changing illumination used single crystal $n\text{-Cd}(\text{Se}, \text{Te})$ as photoanode and a Sn/SnS storage system. The system, described by Licht and Manassen (1987), and shown schematically in Fig. 10.11, was further improved by a series of solution-phase optimisations (caesium electrolyte with low hydroxide, and optimised polysulphide), to provide a higher photopotential (thus requiring only one photocell instead two, as seen by comparing Figs. 10.2 and 10.11) and improved stability, and also the use of single-crystal, rather than thin-film, $\text{Cd}(\text{Se}, \text{Te})$ to improve photopotential and cell efficiency (Licht *et al.*, 1987). The storage and conversion reactions are:



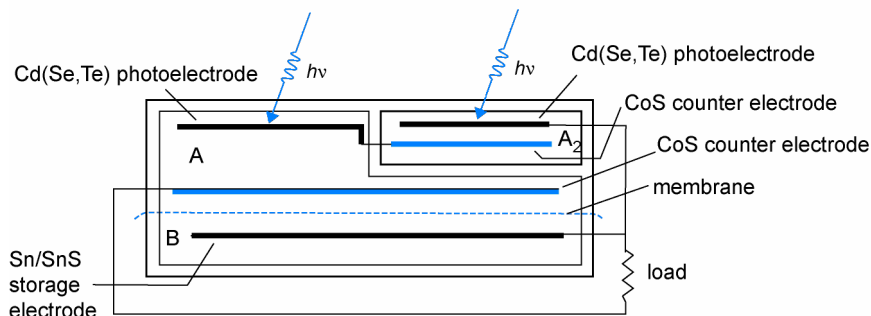


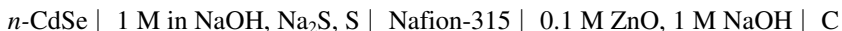
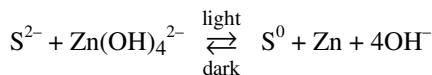
Figure 10.11 A bipolar thin-film n -Cd(Se,Te)-polysulphide-CoS photoelectrochemical solar cell with *in situ* Sn/SnS-CoS storage. Compartments A and A₂ contain alkaline polysulphide solution, and compartment B contains alkaline sulphide solution.

The cell has the design shown in Fig. 10.2 and the cell configuration is:



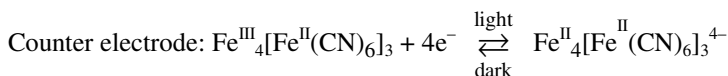
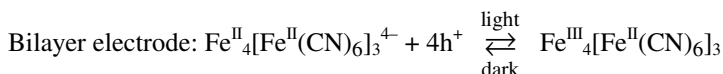
Cell characteristics: PEC power conversion efficiency of 12.7% under 96.5 mW cm^{-2} insolation, and voltage of -1.1 V vs. SHE at maximum power point, sufficient to drive the SnS/Sn storage system. Under direct illumination, the 0.08 cm^2 single crystal photoelectrode generated more than 1.5 mA through the 3 cm^2 SnS electrode, driving SnS reduction while supporting 0.33 mA through a 1500 ohm load simultaneously at a photogenerated voltage of 0.495 V. In the dark, spontaneous oxidation drives the load with a storage efficiency of over 95%. The total conversion efficiency, including conversion and storage losses, was 11.8%.

Other types of storage systems investigated include Cd/Cd(OH)₂ using n -GaAs/polychalcogenide PECs (Ang and Sammells, 1980), and Ni/Ni²⁺ using an n -GaP/ferro(ferri)cyanide PEC (Yonezawa *et al.*, 1981). The use of the well-known Zn/zincate storage couple together with a CdSe/polysulphide PEC was described in detail by Bratin and Tomkiewicz (1980). In this study, three semiconductor PEC devices connected in series drove the storage system. Charging was carried out up to 90% of the capacity, followed by complete discharge. The overall observed charge efficiency was 83%. Even though the system was not fully optimised with respect to photoelectrode, electrolyte and storage, voltage efficiency of 75% was obtained during discharge. Discharge curves were flat until the stored active material was fully consumed. The storage reaction and cell configuration are:



Cell characteristics: polycrystalline photoelectrode, Ni counter electrode, basic cell design based on Fig. 10.5, U_{redox} of $\text{S}_x^{2-}/\text{S}^{2-} = 0.500 \text{ V vs. SHE}$, U_{redox} of $\text{Zn}/\text{Zn}(\text{OH})_4^{2-} = -1.25 \text{ V vs. SHE}$, artificial illumination, conversion efficiency = 3%, photovoltage = 0.75 V, during discharge through 75 ohm load between C and Ni at a discharge current of 10 mA, discharge voltage = 0.6 V.

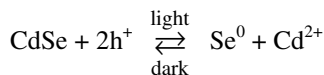
Organic semiconductors have made great strides in recent years, and some promising devices based on them are described in Chapter 7 by Benson-Smith and Nelson. Twenty years ago, organic semiconductors were used as the conversion electrode in a PECS cell, as described by Kaneko *et al.* (1987). The process in this cell is similar to that in a concentration cell. During photocharging, Prussian Blue (PB, $\text{Fe}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$) is reduced at the photocathode and oxidised at the anode. In the dark, the redox process involving PB is reversed, producing an electron flow. Process ability, stability and lack of photocorrosion make these low-bandgap organic materials very attractive for photoelectrochemical applications. However, they are defect-based systems and the very low conversion efficiencies and tendency to self-discharge appear to outweigh these benefits. The storage reaction and cell configuration of the cell of Kaneko *et al.* (1987) are:



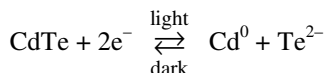
Cell characteristics: Illumination 500 W xenon lamp. The ITO/P3MT (poly-3-methylthiophene) electrode has open-circuit voltage = 0.44 V, short-circuit photocurrent 0.09 $\mu\text{A cm}^{-2}$, charge efficiency of the storage cell = 40%.

Another interesting cell variation devised by Gerritsen and Ruppel (1984) took advantage of photocorrosion to drive a storage cell. Under illumination, *n*-CdSe is decomposed and *p*-CdTe is electroplated; the reverse occurs during cell discharge.

However, photoactivity requires an optimised semiconductor surface, and in an environment where the surface is constantly changed the surface optimisation is lost. This, combined with the poor kinetics of the *p*-type photoreduction, results in a continual deterioration of the photoactivity, and causes low photo-efficiency and discharge power density. The storage reaction at one photoelectrode is:



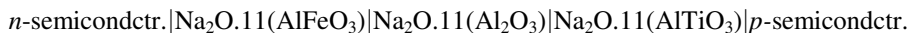
while the other electrode is photoelectroplated by Cd:



The cell configuration is:

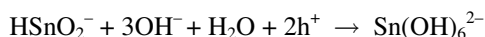


Sammells and Ang (1987) demonstrated a PECS cell employing a solid electrolyte. Metal ions introduced into a solid β -alumina lattice behave like ions in solution. During charging, Fe and Ti change their oxidation states and charge balance is maintained by the migration of Na^+ ions from one phase to the other. In the actual cell design, an *n*-type semiconductor is connected to the alumina phase containing Ti, and *p*-material is connected to the phase containing Fe. Limitations are the comparatively slow diffusion of ions in the solid electrolyte, and resistance to ionic movement at various phase boundaries, which lower the energy output during discharge. In this device, back-wall illumination demands the use of very thin semiconductor layers to minimise absorption losses, and the cell has the general form:



An example of a two-electrode PECS that does not need a membrane is polycrystalline Cd(Se,Te) in an alkaline $\text{Sn}^{2+}/\text{Sn}^{4+}$ electrolyte (G. Hodes, unpublished results). Menezes *et al.* (1977) reported that acidic $\text{Sn}^{2+}/\text{Sn}^{4+}$ electrolyte stabilised CdTe photoelectrodes to some extent. In experiments using polycrystalline Cd(Se,Te) on an exposed (on the back side) Ti substrate, this electrolyte was found to stabilise the photoanode somewhat, but not very efficiently. However, use of alkaline $\text{Sn}^{2+}/\text{Sn}^{4+}$ resulted in considerably improved stability (although still inferior to polysulphide). On illumination, metallic Sn deposited on the exposed backside (the Ti substrate) of the photoelectrode. In the dark, this Sn discharged (current flow in the

same direction as on illumination) through the counter electrode. The photooxidation at CdSe is probably



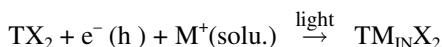
while the reverse reaction occurs at the counter (Pt) electrode. However, some of the electrons generated by the photoreaction go directly to the exposed Ti substrate where Sn metal is formed:



and this tin is reoxidised on discharge in the dark. No membrane is required since the same solution undergoes two different reactions. The Ti substrate is apparently an insufficiently good electrocatalyst for the $\text{Sn}^{\text{IV}}/\text{Sn}^{\text{II}}$ reaction to degrade the photocell performance too much (as is the case for most redox couples), and this is the main reason for using Ti as a substrate in PECs. However, the Ti substrate is good enough for Sn deposition if for no other reason that, once some Sn has been deposited, further deposition occurs on Sn. Apparently Sn is also a poor electrocatalyst for the $\text{Sn}^{\text{IV}}/\text{Sn}^{\text{II}}$ reaction. The standard reduction potentials of the $\text{Sn}^{\text{II}}/\text{Sn}^{\text{IV}}$ couple (-0.93 V) and the $\text{Sn}^{\text{II}}/\text{Sn}^0$ couple (-0.91 V) reactions are almost the same. The cell voltage is therefore very low, although it can be varied somewhat by adjusting the $[\text{Sn}^{\text{II}}]/[\text{Sn}^{\text{IV}}]$ ratio in the solution. The photoelectrode was only moderately stable, so this system was not studied further. However, it does show how a PECS cell might be simplified.

10.5.3 PECS cells incorporating intercalation or other changes in the electrodes

The use of an intercalation reaction is a specific case of solid-phase storage. In photo-intercalation, illumination drives insertion storage into layered compounds (Tributsch, 1986). The photointercalation process can be characterised as



where TX_2 is generally a non-intercalated transition metal dichalcogenide, and $\text{TM}_{\text{IN}}\text{X}_2$ is the intercalated compound. For this process to occur without the assistance of an external power source, a counter electrode is driven at an electrode potential negative to that of the layer-type intercalating electrode. The process is generally restricted to *p*-type materials. The development of this concept has been slow due to dearth of materials that are stable semiconductors, and at the same time behave as

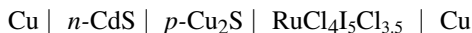
intercalating compounds able to exchange guest ions and molecules with an electrolyte in a reversible manner without disrupting photon absorption.

Betz *et al.* (1987) have described an example of photointercalation. In their cell, U_{redox} of copper thiophosphate is variable depending on the degree of intercalation. Limitations of this system are poor discharge kinetics and low energy density of the discharge. The cell configuration is:



Cell characteristics: U_{redox} of $\text{Cu}^+/\text{Cu}^0 = -0.344$ vs. SHE, illumination 117 mW cm^{-2} Xe lamp, photopotential = 100 mV, charging current $<50 \mu\text{A cm}^{-2}$, discharge current $<10 \mu\text{A cm}^{-2}$.

Tonomura and Teratoshi (1986) have suggested an all-solid-state cell design whose operation depends on the change of electrode potential of $p\text{-Cu}_x\text{S}$ with changes in the composition x . In one example, Cu is oxidised at the $n\text{-CdS}$ surface while Cu^+ is reduced at the Cu electrode during charging. Between the two electrodes, Cu^+ ion transport process takes place in the solid-state electrolyte. The cell configuration is:



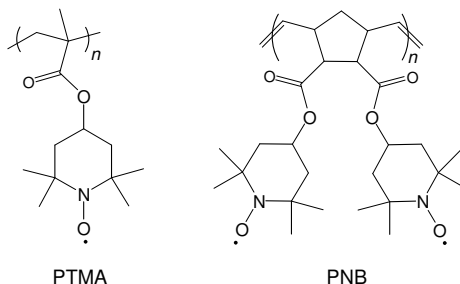
Another example is the following configuration:



These cells must be very thin because light has to travel several layers to reach the junction. The efficiencies of all these cells are very low, but again they demonstrate the wide variation of possible designs.

10.5.4 PECS cells with novel solid-phase storage

Finally in this section, we mention some novel solid-phase storage concepts. The rechargeable ‘Organic Radical Battery’ under development by NEC (Nishide *et al.*, 2004; Nakahara *et al.*, 2007a and 2007b; Suga *et al.*, 2007) makes use of the redox reactions of nitroxide radical polymers for charge storage. Polymers such as poly-(2,2,6,6-tetramethyl-piperidinyloxy-4-yl methylacrylate (PTMA) and the polynorbornene derivative PNB, which contain the redox-active radical 2,2,6,6-tetramethylpiperidiny-*N*-oxy (TEMPO) as the pendant group, have almost stoichiometric charge-storage capability and rapid charge/discharge characteristics. The use of such



polymers in conjunction with a semiconductor photoelectrode in a photoelectrochemical cell with storage is the subject of a patent (Satoh *et al.*, 2003).

Two Japanese groups have combined the Ru-dye-sensitised $\text{TiO}_2/\text{I}^-/\text{I}_3^-$ photoanode of the Grätzel cell with storage electrodes to make PECS, albeit of modest charge-storage capacity. In the three-electrode cell of Nagai and Segawa (2004), illumination of the Grätzel photoanode charges a conducting polypyrrole storage electrode of the same geometric surface area; the latter could store the charge generated by ~ 30 min worth of AM 1.5 insolation. Miyasaka and Murakami (2004) reported a light-driven self-charging two-electrode ‘photocapacitor’ which is essentially a Grätzel cell with the addition of a layer of activated carbon at each electrode, separated by a porous dielectric resin. As Morales-Acevedo (2005) pointed out, the reported capacitance of the device (0.69 F cm^{-2} at a charging voltage of $>0.45 \text{ V}$) is much too low to store the charge generated by even a few hours of normal cell operation. However, these and similar devices could be useful for charge-smoothing.

10.5.5 PECS coupled to external fuel cell

In the early 1980s, Texas Instruments developed an innovative programme based on the hybrid photovoltaic-storage cell shown in Fig. 10.12. This used small doped embedded silicon spheres as photoanode and photocathode, and was designed to provide a close match between the maximum-power voltage and bromine oxidation in acidic solution. The photovoltage of the two types of junction, *p-n* and *n-p*, add to yield a new photovoltage sufficient to split HBR. The programme was discontinued after a few years, but the system has several attractive features, in particular the novel electrode arrangement. In the bromine/embedded Si sphere system, energy, stored as bromine, was recovered in an external hydrogen-bromine fuel cell. Figure 10.12 shows the action of the cell. The conversion and storage reaction and cell configuration of the system can be summarised:

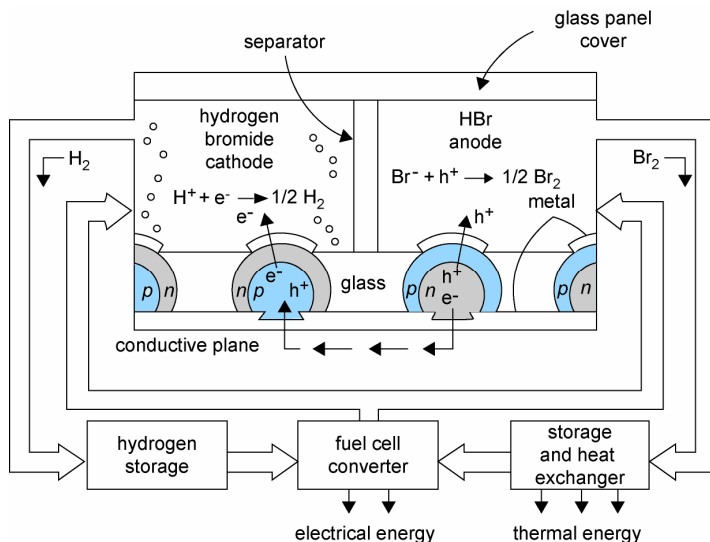
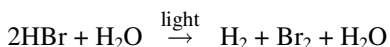


Figure 10.12 Schematic diagram of the Texas Instruments Solar Energy System. Illumination occurs through the electrolyte to produce hydrogen gas, which can be stored as a metal hydride, and bromine, which can be stored as aqueous tribromide. A hydrogen-bromine fuel cell is used to convert chemical to electrical energy and regenerate the hydrogen bromide electrolyte in a closed loop cyclic system. Thermal energy can be extracted through a heat exchanger.



Photoanode: Contact metal | ohmic contact | *n*-Si | *p*-Si | surface metal | solution

Photocathode: Contact metal | ohmic contact | *p*-Si | *n*-Si | surface metal | solution

10.6 High-efficiency multiple-bandgap cells with storage

A limited fraction of incident solar photons have sufficient (greater than bandgap) energy to initiate charge excitation within a semiconductor. Due to the low fraction of short-wavelength solar light, wide-bandgap solar cells generate a high photovoltage, but have low photocurrent. Smaller-bandgap cells can utilise a larger fraction of the incident photons, but generate lower photovoltage. Multiple-bandgap devices can overcome these limitations. In stacked multijunction systems, the topmost cell absorbs (and converts) energetic photons, but is transparent to lower energy photons,

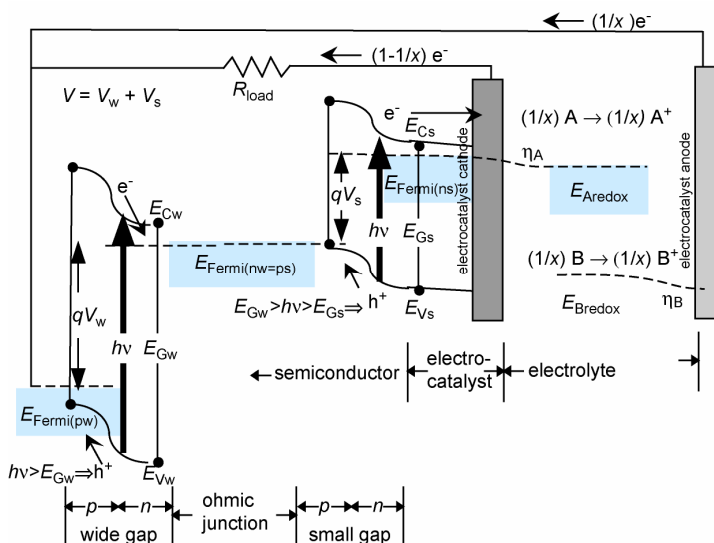


Figure 10.13 Energy diagram for a bipolar-bandgap indirect ohmic storage multiple-bandgap photoelectrochemical solar cell (MBPEC) (Licht *et al.*, 1998 and 1999).

which are absorbed by subsequent layer(s). Conversion efficiencies can be enhanced, and calculations predict that a two-bandgap system, with 1.64 eV and 0.96 eV bandgaps, would have an ideal efficiency of 38% and 50%, for 1 and 1000 Suns concentration, respectively. The ideal efficiency increases to a limit of 72% for a 36-bandgap solar cell (Henry, 1980). In other calculations, higher ideal efficiencies for a two-bandgap cell of 66–72% have been cited (Landsberg and Tonge, 1980; Ross and Nozik, 1982; Haught, 1984).

High solar conversion and storage efficiencies have been attained with a system that combines efficient multiple-bandgap semiconductors with simultaneous high capacity electrochemical storage. Figure 10.13 shows the energy diagram for one of several multiple-bandgap cells, and other configurations are also feasible (Licht *et al.*, 1998a, b and c). Storage occurs at the potential $U_{redox} = U_{Aredox} - U_{Bredox}$, where $U_{Aredox} = U_{A+/A}$, *etc.* On illumination, two photons generate each electron, a fraction $1/x$ of which drives a load, while the remainder $(1 - 1/x)e^-$ charges the storage redox couple. Without light, the potential falls below U_{redox} and the storage couple discharges spontaneously. This dark discharge is directed through the load, rather than through the multijunction semiconductor's high dark resistance.

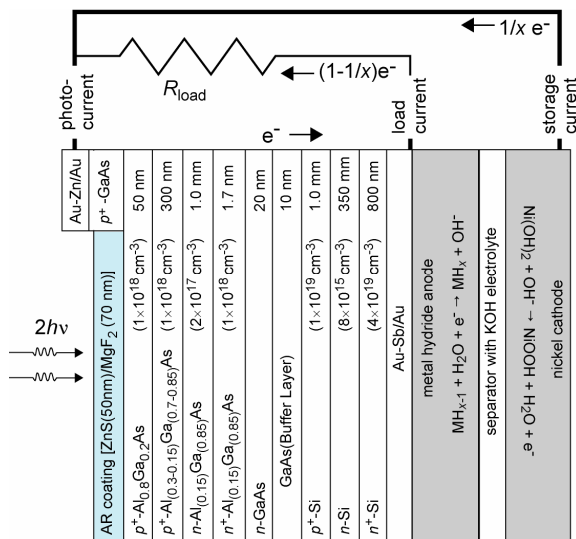
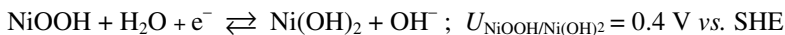
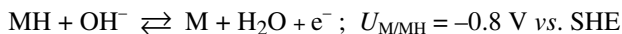


Figure 10.14 The bipolar AlGaAs | Si | MH | NiOOH MBPEC solar cell (Licht, 1999).

Figure 10.14 shows an operational form of the cell with the energy diagram of Fig. 10.13 (Licht *et al.*, 1999). The cell contains both multiple bandgap and electrochemical storage and, unlike a conventional photovoltaic cell, provides a nearly constant energy output in illuminated *and* dark conditions. The cell combines bipolar AlGaAs ($E_g = 1.6$ eV) and Si ($E_g = 1.0$ eV) and AB₅ metal hydride/NiOOH storage. Lattice matching between AlGaAs and Si is critical to minimise the dark current, provide ohmic contact without light absorption loss, and maximise cell efficiency. The NiOOH/MH storage process is nearly ideal for the AlGaAs/Si combination due to the excellent match of the storage and photocharging potentials. The storage processes involve MH oxidation and nickel oxyhydroxide reduction:



As shown in Fig. 10.15, the cell generates a light-variation insensitive potential of 1.2–1.3V at a total solar-to-electrical energy conversion efficiency (including storage losses) of over 18%. In a variation on this spectacular device, Licht *et al.* (1999) built a regenerative photoelectrochemical solar cell of record 19.1% efficiency using a solution-phase $\text{V}^{3+}, \text{V}^{2+}$ redox couple instead of the storage electrode. In another

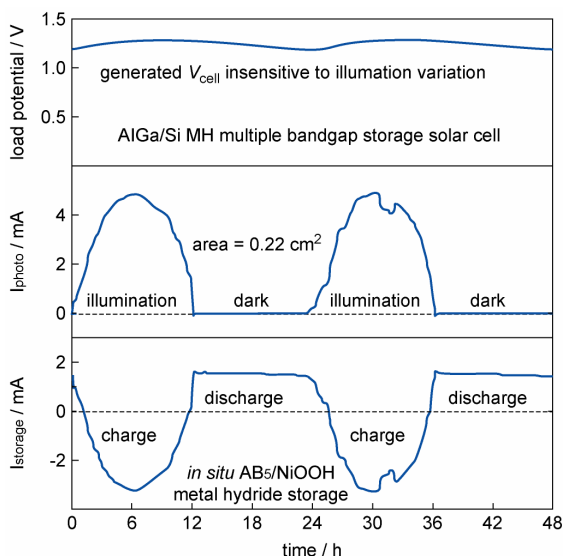


Figure 10.15 Two days' measured conversion and storage characteristics of the AlGaAs/Si/MH/NiOOH MBPEC solar cell (Licht, 1999).

variation Licht (2001, 2003) paired the multiple-bandgap photocathode with a $\text{RuO}_2/\text{Pt}_{\text{black}}$ anode to photoelectrolyse water with >18% solar-to-hydrogen conversion efficiency.

10.7 Conclusions

Conversion and storage of solar energy is of growing importance as fossil fuel energy sources are depleted and stricter environmental legislation is implemented. Photoelectrochemical systems have the potential not only to convert, but also to store, incident solar energy. Design component and system considerations, and a number of photoelectrochemical solar cells with storage have been reviewed in this chapter. Future advances in photoelectrochemical storage will be driven not only by technological developments, but also by economic (fossil fuel prices) and environmental (greenhouse gas build-up) factors.

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CHAPTER 11

MEASURING ULTRAFAST PHOTOINDUCED ELECTRON-TRANSFER DYNAMICS

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There is more to life than increasing its speed.

Mahatma Ghandi (1869–1948)

11.1 Introduction

Novel hybrid solar cells based on composites of molecular and nanostructured semiconductor components have attracted significant interest as potential low cost alternatives to traditional photovoltaic (PV) cells, as discussed in several chapters of this book. Among the most successful and promising examples are cells based on dye-sensitised nanocrystalline thin film (O'Regan and Grätzel, 1991; Bach *et al.*, 1998) and conjugated polymer/nanoparticles or quantum dots (Huynh *et al.*, 2002) and C₆₀ composites (Shaheen *et al.*, 2001). For example, in dye-sensitised solar cells that are based on Ru(dcbpy)₂(NCS)₂ [dcbpy = (4,4'-dicarboxy-2,2'-bipyridine)] (N3)-sensitised nanocrystalline TiO₂ thin films, a solar-to-electric power conversion efficiency of about 10% has been reported (O'Regan and Grätzel, 1991; Nazeeruddin *et al.*, 1993). A key feature of these nanocomposites is the large effective interface area, which allows for high light-harvesting efficiency while maintaining thin junctions (Hagfeldt and Grätzel, 1995). The latter is essential for efficient charge separation across the interface within the limited excited-state lifetime (Hagfeldt and Grätzel, 1995; Gregg, 2003). Indeed, extensive recent studies on N3-sensitised TiO₂ nanocrystalline thin films have revealed ultrafast electron injection from the photoexcited sensitisers to the semiconductor, with the majority of the injection

occurring in <100fs (Tachibana *et al.*, 1996; Hannappel *et al.*, 1997; Ellingson *et al.*, 1998; Ellingson *et al.*, 1999; Asbury *et al.*, 1999a; Haque *et al.*, 2000; Heimer *et al.*, 2000; Tachibana *et al.*, 2001; Asbury *et al.*, 2001a; Asbury *et al.*, 2001b; Benko *et al.*, 2002; Kallonen *et al.*, 2002; Kuciauskas *et al.*, 2002; Asbury *et al.*, 2003). Ultrafast electron injection, combined with a much slower back electron transfer (Nelson, 1999; Haque *et al.*, 2000; Nelson *et al.*, 2001), is essential for achieving the high (almost unity at peak wavelength) incident-photon-to-current conversion efficiency in these devices (Hagfeldt and Grätzel, 1995).

Because of its fundamental importance and crucial role in improving the efficiency of novel hybrid solar cells, electron-transfer (ET) dynamics at the molecule–nanoparticle interface have been intensively studied by many research groups in recent years (Kamat, 1993; Kamat, 1994; Lanzafame *et al.*, 1994; Hagfeldt and Grätzel, 1995; Miller *et al.*, 1995; Kamat *et al.*, 1996; Nozik and Memming, 1996; Tachibana *et al.*, 1996; Cherepy *et al.*, 1997; Hannappel *et al.*, 1997; Heimer and Heilweil, 1997; Kamat and Meisel, 1997; Ellingson *et al.*, 1998; Hasselmann and Meyer, 1999; Martini *et al.*, 1999; Gaal and Hupp, 2000; Haque *et al.*, 2000; Heimer *et al.*, 2000; Huber *et al.*, 2000; Iwai *et al.*, 2000; Galoppini *et al.*, 2001; Nelson *et al.*, 2001; Asbury *et al.*, 2001a; Kallonen *et al.*, 2002; Kuciauskas *et al.*, 2002; Olsen *et al.*, 2002; Persson *et al.*, 2002; Schnadt *et al.*, 2002; Stier and Prezhdo, 2002; Furube *et al.*, 2003; Piotrowiak *et al.*, 2003; Anderson and Lian, 2004).

Figure 11.1 shows a cartoon of photoinduced electron transfer at the molecule–semiconductor nanoparticle junction. The junction can be considered as a donor–bridge–acceptor complex with a sensitiser (electron donor) anchored to the semiconductor nanoparticle (electron acceptor) surface through a molecular spacer and anchoring group (bridge). Optical excitation of the sensitiser to its molecular excited states initiates electron injection (forward ET) from these states into the semiconductor conduction band through the mediating bridge. This process competes with other non-radiative and radiative decay pathways of the excited sensitiser. Because of the limited excited-state lifetimes of molecular sensitisers, efficient charge separation requires ultrafast electron injection on the subnanosecond and faster time scale. Measurement of the dynamics of this process and understanding the factors influencing its rate are the major focus of this chapter. The injected electron may recombine with the oxidised adsorbate in the process of back ET, which competes with electron relaxation and transport processes in the nanoparticles. As a result, the back ET processes are often highly non-single-exponential and much slower. A complete characterisation of this process demands techniques that can extend into the microsecond to millisecond time scale, and are quite different from the measurement of ultrafast injection process. For reviews of back ET studies, the reader is referred to

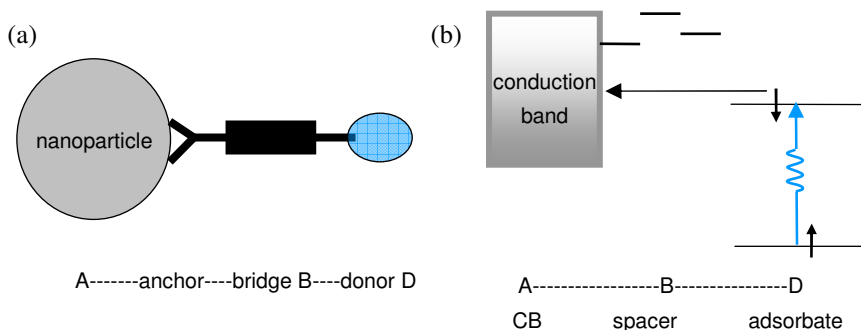


Figure 11.1 Photoinduced electron transfer from molecules to semiconductor nanoparticles. (a) Depiction of a donor–bridge–acceptor system; (b) schematic diagram of relevant orbitals.

several studies and reviews (Hasselmann and Meyer, 1999; Nelson, 1999; Martini *et al.*, 1999; Gaal and Hupp, 2000; Haque *et al.*, 2000; Nelson *et al.*, 2001; Barzykin and Tachiya, 2002; Kilsa *et al.*, 2003; Nelson *et al.*, 2004).

The rest of this chapter is organised as follows: experimental techniques for measuring interfacial electron-transfer rates are described in Section 11.2, and Section 11.3 summarises theoretical descriptions and current experimental results.

11.2 Techniques for measuring ultrafast electron transfer

Most of the early investigations of interfacial ET rates were based on electrochemical current or voltage measurements (Lewis, 1991; Miller *et al.*, 1995; Nozik and Memming, 1996; Sachs *et al.*, 1997). The advantages and limitations of these methods are detailed in Chapter 12. It is often difficult to measure ET rates on the sub-nanosecond timescale with these techniques. For ET in this ultrafast regime, techniques based on direct ultrafast time-resolved spectroscopy are now extensively used. A comprehensive description of the method and application of ultrafast spectroscopy can be found in text books (Fleming, 1986; Rulliere, 2003). In this section, we describe some techniques that have been used for interfacial ET studies.

11.2.1 Time-resolved fluorescence

Time-resolved fluorescence spectroscopy has been used to probe ultrafast interfacial electron transfer since the 1970s (Gerischer and Willig, 1976; Sakata *et al.*, 1990; Willig *et al.*, 1990; Miller *et al.*, 1995; Heimer and Meyer, 1996; Rehm *et al.*, 1996).

In this approach, the excited-state lifetime of molecules is measured by following the decay of their fluorescence. The electron injection rate (k_{inj}) is calculated from the measured fluorescence decay rate (k_{obs}) and the intrinsic radiative (k_{f}) and non-radiative (k_{nr}) excited decay rates through the relationship

$$k_{\text{obs}} = k_{\text{inj}} + k_{\text{f}} + k_{\text{nr}} \quad (11.1)$$

The advantage of this technique is the excellent sensitivity of fluorescence detection, which can readily reach the single-photon level. However, it does not identify charge-transfer products directly. Instead, the ET process is inferred from quenching of the fluorescence quantum yield and the rate is calculated from the shortened excited-state lifetime of the molecules. The quantification of ET rates requires the knowledge of the radiative and non-radiative rates, which are often determined in non-ET but otherwise similar environments. However, both quantities are sensitive to the environment, making this a challenging task (Chance *et al.*, 1975; Lukosz and Kunz, 1977; Waldeck *et al.*, 1985; Hellen and Axelrod, 1987). The radiative rate varies with the dielectric environment (Chance *et al.*, 1975; Arias *et al.*, 1982) and molecule orientation at the interface (Lukosz and Kunz, 1977; Hellen and Axelrod, 1987; Macklin *et al.*, 1996). The non-radiative rate is also dependent on the viscosity, rigidity and polarity of the environment for molecules whose decay pathways involve significant structural rearrangement (Fleming and Hanggi, 1993). For example, in rhodamine B and related molecules, the extent of non-radiative decay via the intramolecular twisted charge-transfer excited state depends on solvent polarity (Casey and Quitevis, 1988), and can be suppressed in a rigid environment (Karstens and Kobs, 1980; Casey and Quitevis, 1988). For interfacial electron transfer, dye aggregation at the interface presents another difficult challenge, since the effect on the radiative and non-radiative decay rates depends on the degree of aggregation (Miller *et al.*, 1995).

The most commonly used and simplest time-resolved fluorescence technique is time-correlated single-photon counting, but this has limited time resolution of about 25 ps (Fleming, 1986). To achieve better time resolution, streak camera or gated fluorescence detection methods can be used (Fleming, 1986; Uehringa *et al.*, 2003). There have been reports of streak camera measurements with time resolutions of ~ 2 ps (Uehringa *et al.*, 2003). In one of the earliest direct time-resolved measurements of interfacial ET, streak camera detection was used to study electron injection from cresyl violet to SnS_2 electrodes (Willig *et al.*, 1990). However, this technique has not been widely used for interfacial studies and we shall not discuss it; Fleming (1986) and O'Connor and Phillips (1984) give an introduction. The best time resolution in

fluorescence detection is achieved through gated detection, to which there are two approaches: fluorescence upconversion and Kerr gate detection (Fleming, 1986).

Time-correlated single-photon counting The most commonly used fluorescence lifetime measurement technique is time-correlated single-photon counting (TCSPC). The principle of this method has been detailed in books by Fleming (1986) and O'Connor and Phillips (1984) and here we give only a brief summary. In this approach, the sample is illuminated with short laser pulses, and the resulting fluorescence photons are detected one at a time. For each detected photon, its delay time, relative to when the molecules are excited, is recorded. A histogram of delay times for detected photons is then constructed. Since the probability of emitting a photon is proportional to the populations of molecules in the excited state at any given delay time, the decay time histogram reflects the population decay kinetics of excited molecules (O'Connor and Phillips, 1984). The time resolution of the technique is determined by the pulse width of the laser and the response time of the detector and photon-counting board. With a microchannel plate photomultiplier tube (MCP-PMT), such as Hamamatsu model R3809U, an instrument response of ~25 ps full-width-at-half-maximum can be achieved (O'Connor and Phillips, 1984; Fleming, 1986).

Fluorescence upconversion In fluorescence upconversion, the fluorescence photons are converted to higher energy photons by sum-frequency mixing with a gate laser pulse in a non-linear crystal. Only fluorescence photons in the time window of the gate laser pulse are upconverted and detected. By scanning the delay time between the gate and the excitation pulses, the fluorescence intensity as a function of delay time can be recorded, producing the excited-state population decay kinetics. The time resolution of this technique is determined by the pulse widths of the exciting and gating lasers (which are often derived from the same source). Time resolution on the ~100 fs level has been achieved (Fleming, 1986; Rosenthal *et al.*, 1991). This technique has been used to measure interfacial ET dynamics in C343-sensitised TiO₂ nanoparticles (Rehm *et al.*, 1996). The superior time resolution comes with a sacrifice of sensitivity. As expected for a non-linear process, the sensitivity of gated detection is much worse than that of direct detection of fluorescence photons.

Optical Kerr gating In optical Kerr gating, fluorescence photons are passed through a Kerr gate that is inserted between two cross polarisers (Fleming, 1986; Arzhantsev and Maroncelli, 2005). An optical gating pulse excites the Kerr gate to change its birefringence through the optical Kerr effect for a short time interval during which the fluorescence photons can pass through the cross polarisers and be detected. By

scanning the delay time of the gate pulse, fluorescence at different delay times can be detected. The temporal width of the Kerr gate is determined by the convolution of the pulse width and the Kerr response of the gate materials. In recent experiments using solid and liquid nonlinear materials, instrument response times of a few hundred femtoseconds have been achieved (Arzhantsev and Maroncelli, 2005).

11.2.2 Transient absorption spectroscopy

General principle Transient absorption spectroscopy is ideally suited for studying interfacial electron-transfer processes in nanoporous materials. The large interfacial area in these materials allows a high effective adsorbate concentration, whose absorption spectrum can readily be measured by static and time-resolved absorption spectroscopy. Transient absorption spectroscopy allows a direct measurement of reactants and products of ET through spectroscopic identification of various species (ground, excited, reduced and oxidized forms) over a wide range of timescales. Modern ultrafast laser technology has rendered transient absorption spectroscopy the most commonly used technique for the study of ultrafast interfacial ET. To achieve time resolutions of nanoseconds and shorter, the pump/probe scheme is often used (Fleming, 1986). In this approach, shown in Fig. 11.2, an UV/visible pump pulse is

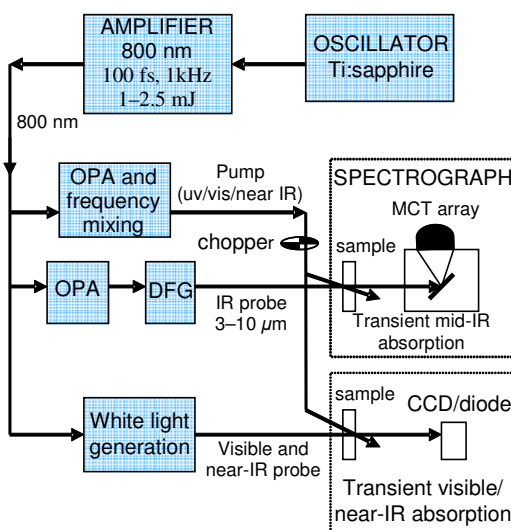


Figure 11.2 Typical set-ups for tuneable femtosecond pump/probe transient absorption spectrometers in mid-IR and visible/near IR.

used selectively to excite the adsorbate molecules, initiating the ET reaction. The subsequent spectral change at some delay time, defined as the arrival time difference between the pump and probe pulse at the sample, is recorded using the probe pulse. The delay time is varied by passing the pump pulse (or the probe pulse) through an optical delay line, which controls the optical path length of the pulse using a translational stage with micrometre or submicrometre precision (light travels $0.3\text{ }\mu\text{m}$ in 1 fs in vacuum). By scanning the delay line, the spectral changes associated with the reactant(s) and product(s) of ET are measured as function of delay time (typically up to $\sim 1\text{ ns}$), from which the dynamics and kinetics of the ET reaction are obtained.

One of the most commonly used sub-picosecond transient absorption spectroscopy setup is based on regeneratively amplified Ti:sapphire systems (Rulliere, 2003). Although output pulse energy and repetition rates vary in different systems, the basic scheme is as shown in Fig. 11.2 (Ghosh *et al.*, 1998b; Wang *et al.*, 2000). The Ti:sapphire regenerative amplifier produces 800 nm output pulses of energy 1 mJ/pulse and full-width-half-maximum (FWHM) of $\sim 100\text{ fs}$ at 1 kHz repetition rate. Similar laser systems with output pulse energies of over 2 mJ are now commercially available. The amplifier output is split into two parts to generate the pump and probe pulses. The wavelength of the pump pulse is typically in the visible and near UV region for photoinduced electron transfer at molecule/semiconductor nanoparticle interfaces. It is chosen to selectively excite the molecules and not the semiconductor, so it is desirable to have a tuneable pump source. This can be generated from an 800 nm pulse by optical parametric amplification (OPA) and subsequent sum-frequency and second harmonic generation of its tuneable signal and idler pulses.

The probe wavelength is chosen such that the reactants and products of ET process can be unambiguously monitored. Two types of transient absorption spectroscopy are often used, one using visible/near-IR probe wavelengths, and the other using mid-IR probes. Tuneable probe beams in the visible/near IR region can be obtained by white light generation or optical parametric amplification (Fleming, 1986; Rulliere, 2003). The probe can be spectrally filtered and detected by a photodiode at selected wavelengths. Since the white-light-generated probe pulse has a broad spectrum covering the visible and near-IR range, it allows broadband detection using a spectrograph and CCD detector (Rulliere 2003). To generate tuneable mid-IR probes, the 800 nm pulse is used to pump an optical parametric amplifier. Difference-frequency mixing of its near-IR signal and idler outputs in an AgGaS_2 crystal generates tuneable mid-IR probe pulses in the wavelength range $3\text{--}10\text{ }\mu\text{m}$. The probe pulse is then spectrally dispersed and recorded with mid-IR single-element or array detectors, many of which are based on Cd(Hg)Te (Wang *et al.*, 2000).

Visible and near IR probe Transient absorption spectroscopy probing in the visible/near-IR region has been used to investigate adsorbate/semiconductor nanocomposite systems by many research groups (Kamat *et al.*, 1996; Cherepy *et al.*, 1997; Hannappel *et al.*, 1997; Hasselmann and Meyer, 1999; Martini *et al.*, 1999; Chikan *et al.*, 2000; Gaal and Hupp, 2000; Huber *et al.*, 2000; Weng *et al.*, 2000; Benko *et al.*, 2002; Kuciauskas *et al.*, 2002; Tachibana *et al.*, 2002; Furube *et al.*, 2003; Piotrowiak *et al.*, 2003). This technique measures electronic absorptions of adsorbate molecules (in ground, excited and oxidised states), stimulated emission from excited states, and absorption of the injected electrons in the semiconductor. The electron-injection dynamics can be monitored through the decay of the reactant (adsorbate excited state) and the rise of the products (oxidised adsorbate or the injected electrons in the semiconductor). Back-electron-transfer kinetics can be measured through the decay of ET products and the regeneration of the ground state, although the latter can also be caused by the decay of excited states through non-ET pathways. However, the technique has some accompanying challenges: there are often spectral overlaps between different species, and spectral shifts caused by non-ET dynamics (such as vibrational and electronic relaxation and solvation) at early times. To determine ET dynamics accurately, it is desirable to record the evolution of the electronic spectra of these species, from which spectral fitting can be used to separate the dynamics of the overlapping species (Zimmermann *et al.*, 2001; Benko *et al.*,

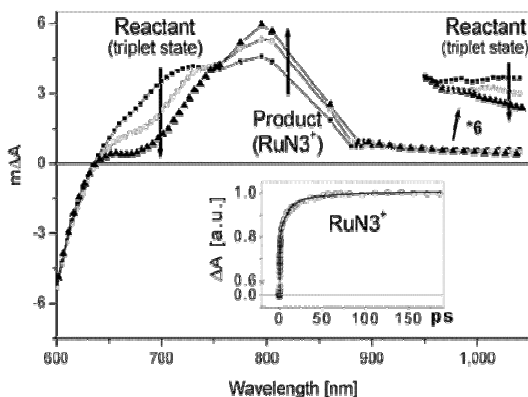


Figure 11.3 Visible and near-IR transient absorption spectra of N3-sensitized TiO₂ film at time delays of 0.5 (■), 10 (○), and 150 ps (▲) between the pump and probe pulses. Clear spectral signatures of triplet excited state and oxidised dye with corresponding dynamics were observed. Inset: transient absorption kinetics of oxidised N3 cation-TiO₂ measured at 860 nm. Symbols are measured data, while the curve is a fit with the following time constants and amplitudes: rise within the laser pulse (20 ± 5%), 28 ± 3 fs (50%), 1 ± 0.1 ps (11%), 9.5 ± 1 ps (12%), and 50 ± 5 ps (7%). Reprinted with permission from *J. Am. Chem. Soc.* **124**, 489 (2002), Fig. 2. Copyright (2002) American Chemical Society.

2002; Benko *et al.*, 2004). Furthermore, anisotropy of the absorption signal can also be used to differentiate these species, as they often have different transition-dipole moment directions (Martini *et al.*, 1998). Shown in Fig. 11.3 is an example of a careful transient absorption study of N3/TiO₂ (Benko *et al.*, 2002; Kallioinen *et al.*, 2002). By measuring the transient spectral evolution of the reactant (adsorbate excited states) and products (cation and injected electrons) over the visible and near-IR range, the injection kinetics (shown in the inset) were unambiguously determined.

Mid-IR probe Transient mid-IR absorption spectroscopy probes vibrational transitions of the adsorbate molecule (ground, excited and oxidised forms) as well as absorption of injected electrons in the semiconductor. The measured IR electron absorption signal may originate from free-carrier absorption, intrasubband transitions or trap absorption (Pankove, 1975). For free-carrier absorption, the absorption coefficient increases with wavelength (λ^α , $\alpha \sim 2-4$). Although their cross sections vary, these signals are present in all semiconductor materials. Therefore, mid-IR transient absorption can be used to study interfacial ET to a wide range of semiconductor materials. In addition to the injected electron, corresponding dynamics of the adsorbate can be simultaneously obtained when the adsorbate molecules have strong vibrational transitions (Anderson and Lian, 2005a). In these cases, transient spectra shows narrow vibrational transitions of the adsorbate (with FWHM of a few to tens of cm^{-1}) superimposed on the broad absorption signal of the injected electrons (Ghosh *et al.*, 1998b; Asbury *et al.*, 2000; Ai *et al.*, 2004). This technique has been used to study electron-injection dynamics from various molecular adsorbate to many semiconductor nanoparticles, such as TiO₂, SnO₂, Sb:SnO₂, ZnO, In₂O₃ and Nb₂O₅. (Ellingson *et al.*, 1998; Ghosh *et al.*, 1998b; Asbury *et al.*, 1999b; Asbury *et al.*, 2000; Anderson *et al.*, 2001; Asbury *et al.*, 2001a; Asbury *et al.*, 2001b; Ai *et al.*, 2003; Asbury *et al.*, 2003; Anderson *et al.*, 2003a; Anderson *et al.*, 2003b; Ai *et al.*, 2004; Anderson and Lian, 2004).

Figure 11.4a shows typical transient absorption spectra probed in the mid-IR for ReC1P (see Fig. 11.7) on TiO₂ in pH 9 buffer. The transient spectra consist of a bleach of the ground state CO stretching band at $\sim 2040\text{cm}^{-1}$ and the absorption band of the excited state at $\sim 2060\text{cm}^{-1}$ and the oxidised form at $\sim 2090\text{cm}^{-1}$. The evolution of the spectra shows the decay of the excited-state peak and the corresponding growth of the oxidised adsorbate peak and the broad absorption signal of electrons, indicating the injection of electrons from the adsorbate excited state into TiO₂. As shown in Fig. 11.4b, the injection kinetics can be obtained by monitoring the growth of the oxidised peak area and/or the injected electron signals, which show good agreement with each other.

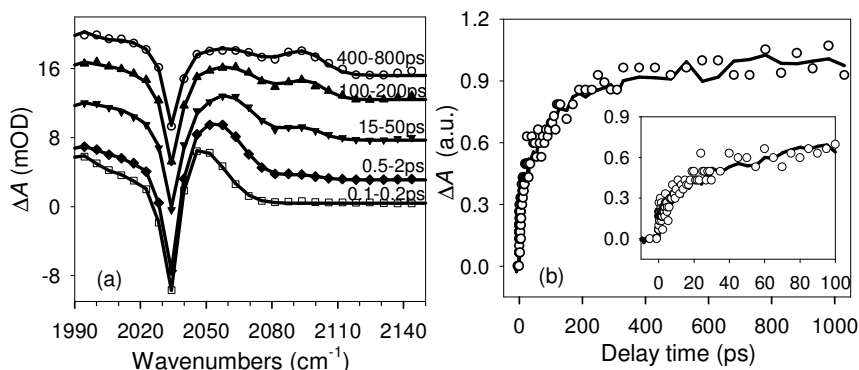


Figure 11.4 (a) Transient IR absorption spectra of ReC1P/TiO₂ in pH 9 buffer at various delay time windows after 400 nm excitation. The symbols are experimental data and lines are fits of the spectrum. (b) A comparison of the growth of the electron absorption signal (line) and the oxidised adsorbate peak area (symbols) obtained from the fit to Fig. 11.4a. The inset shows the same data at early delay times. Reprinted with permission from *J. Phys. Chem. B* **109**, 19345 (2005). Copyright (2002) American Chemical Society.

11.2.3 New experimental approaches

While transient absorption and time-resolved fluorescence are the most commonly used techniques for studying interfacial ET, there is a need for new techniques that probe different aspects of these processes. Some new approaches have been developed, although not as yet extensively used. These new techniques offer exciting possibilities of new insight into interfacial ET. For example, transient terahertz probes allow the determination of the dynamics of injected electrons in the nanoparticle (Beard *et al.*, 2002; Turner *et al.*, 2002). Single-molecule fluorescence spectroscopy provides insight into the nature of heterogeneous distribution in interfacial ET (Lu and Xie, 1997; Holman *et al.*, 2003; Biju *et al.*, 2004; Goh *et al.*, 2005). Most absorption based techniques requires a large surface adsorbate concentration, and are not applicable to ET on a single-crystal surface. Measuring ET dynamics at single-crystal surfaces provides a simpler model system that is helpful for a more detailed understanding of interfacial ET. In this regard, techniques that are surface-restricted, such as surface-restricted grating (Kasinski *et al.*, 1989; Lanzafame *et al.*, 1994) or surface selective, such as second harmonic generation (SHG) or sum-frequency generation (SFG) (Shen, 1984; Eienthal, 1996a; Eienthal, 1996b; Richmond, 2001; Chen *et al.*, 2002; Richmond, 2002), should be applicable. In this section, the main features of these techniques are introduced.

Transient terahertz spectroscopy Time-resolved terahertz (THz) spectroscopy (TRTS) has been used to measure the transient photoconductivity of injected electrons in dye-sensitised titanium oxide with subpicosecond time resolution (Beard *et al.*, 2002; Turner *et al.*, 2002). Terahertz probes cover the far-infrared ($10\text{--}600\text{ cm}^{-1}$ or $0.3\text{--}20\text{ THz}$) region of the spectrum and measure frequency-dependent photoconductivity. The sample is excited by an ultrafast optical pulse to initiate electron injection and subsequently probed with a THz pulse. In many THz detection schemes, the time-dependent electric field $\mathcal{E}(t)$ of the THz probe pulse is measured by free-space electro-optic sampling (Beard *et al.*, 2002). Both the amplitude and the phase of the electric field can be determined, from which the complex conductivity of the injected electrons can be obtained. Fitting the complex conductivity allows the determination of carrier concentration and mobility. The time evolution of these quantities can be determined by varying the delay time between the optical pump and THz probe pulses. The advantage of this technique is that it provides detailed information on the dynamics of the injected electrons in the semiconductor and complements the time-resolved fluorescence and transient absorption techniques, which often focus on the dynamics of the adsorbates. A similar technique, time-resolved microwave conductivity, has been used to study injection kinetics in dye-sensitised nanocrystalline thin films (Fessenden and Kamat, 1995). However, its time resolution is limited to longer than 1 ns.

Single-molecule fluorescence The single-photon sensitivity of fluorescence detection methods allows the study of ET in samples with low adsorbate concentration. Study of ET on single-crystal surfaces should be possible (Willig *et al.*, 1990). This also suggests the possibility of measuring fluorescence lifetimes (and therefore ET rates) of single molecules. There have been four reported single-molecule interfacial ET studies in recent years (Lu and Xie, 1997; Holman *et al.*, 2003; Biju *et al.*, 2004; Goh *et al.*, 2005). This technique offers exciting possibilities to reveal the nature of inhomogeneous distribution hidden under the highly non-single-exponential ET kinetics observed in ensemble average measurements (Anderson and Lian, 2005a). The key difference from ensemble-averaged fluorescence measurements is to ensure that there is only one molecule in the laser excitation volume. This can be accomplished by focusing the excitation pulse to a diffraction limit spot with microscope objectives and reducing the surface coverage of the fluorescence molecules to the $\ll 1\text{ }(\mu\text{m})^{-2}$ level. The microscope objective also allows fluorescence collection over a large solid angle, enhancing the detection efficiency. In the reported single-molecule interfacial ET studies, the fluorescence lifetime was measured by the time-correlated single-photon-counting technique using avalanche photodiodes as the

detector (Lu and Xie, 1997; Biju *et al.*, 2004; Goh *et al.*, 2005). The typical time resolution of this setup is about 400ps, and time resolution down to ~60 ps has been reported for single-molecule ET measurements using a special avalanche photodiode (Yang *et al.*, 2003). In addition to the limited time resolution, measuring fast ET by single-molecule fluorescence is also challenging in that the ET process quenches fluorescence. Molecules undergoing faster ET emit fewer fluorescence photons. As a result, it is still difficult to measure ultrafast single-molecule ET on the <10 ps time scale (Lu and Xie, 1997; Goh *et al.*, 2005).

Surface-restricted grating The surface-restricted grating method has been demonstrated as a powerful probe of reaction dynamics at semiconductor single-crystal surfaces (Kasinski *et al.*, 1989; Lanzafame *et al.*, 1994). This technique is based on nonlinear four-wave mixing. Two time-coincident excitation pulses are crossed at the surface to generate a spatially sinusoidal interference pattern on the surface. The pattern of light intensity leads to a corresponding spatial pattern of electron-hole pairs and free-carrier density, which generates a sinusoidal spatial pattern in the material refractive index, forming a grating. By measuring the diffraction efficiency of the transient grating as a function of the probe/pulse delay time, the carrier population and dynamics can be determined, providing a way to monitor interfacial electron-transfer dynamics. Since the penetration depth of the excitation beam is limited, the grating is restricted to the surface of the crystal and only the carriers at and near the surface are studied. This approach was used to study interfacial electron transfer at the single-crystal n -TiO₂/H₂O liquid interface (Kasinski *et al.*, 1989).

Second-harmonic or sum-frequency probe Second-harmonic generation (SHG) and sum-frequency generation (SFG) are techniques that can selectively probe the bulk solid/liquid interface at the molecular level (Shen, 1984; Eisenthal, 1996a; Eisenthal, 1996b; Richmond, 2001; Chen *et al.*, 2002; Richmond, 2002). These non-linear second-order processes are electric-dipole-forbidden in centrosymmetric media, such as bulk solution, but are allowed at interfaces. As a result, SFG and SHG are interface-selective probe techniques (Shen, 1984). In an SFG measurement, two input beams, centred at ω_1 and ω_2 (for SHG, $\omega_1 = \omega_2$), overlap at the interface and generate an output beam at the sum frequency $\omega_1 + \omega_2$. The intensity of the SFG signal depends on the adsorbate population and orientations, and their resonance frequencies reveal the molecular electronic or vibrational energy levels. Their polarisation dependence can be used to determine the geometry of the adsorbate relative to the surface. So far these techniques have been used mainly for probing static properties of various interfaces, including the TiO₂/liquid interface (Lantz *et al.*, 1993; Liu *et al.*,

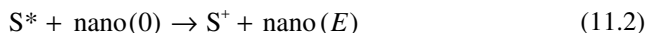
1999; Wang *et al.*, 2003; Wang *et al.*, 2004). The time resolution of this technique is inversely proportional to the spectral resolution. With 10 cm^{-1} spectral resolution, a time resolution of $\sim 1.5\text{ ps}$ can be obtained. These probe techniques can be combined with an excitation pulse in a pump/probe scheme to measure interface selective dynamics. They have been used to study solvation dynamics at a liquid-liquid interface (Zimdars *et al.*, 1999) and vibrational relaxation on a metal surface (Bonn *et al.*, 2000; Bonn *et al.*, 2001). Although not yet reported, the technique should also be applicable to the study of interfacial electron-transfer dynamics.

11.3 Current understanding of ultrafast electron transfer

11.3.1 Theoretical model

The basic theoretical framework for describing electron transfer in bulk solid/liquid interfaces was developed in the 1960s (Marcus, 1965; Gerischer, 1970; Levich, 1970). Fundamentally, photoinduced electron injection from the molecular excited state to a semiconductor nanoparticle can be described as electron transfer from a discrete and localised molecular state to a continuum of delocalised $\mathbf{k}$ states in the semiconductor. As shown in Fig. 11.5, the reactant state corresponds to the electron in the molecular excited state and the product states correspond to the oxidised molecule and the transferred electron in the semiconductor conduction band. There is a continuous manifold of product states, corresponding to the injected electron at different electronic levels in the semiconductor.

In the non-adiabatic limit, the total ET rate can be expressed as the sum of ET rates to all possible accepting states in the semiconductor (Marcus, 1965; Gao *et al.*, 2000; Gao and Marcus, 2000; Gosavi and Marcus, 2000). For electron injection from an adsorbate excited state with electrochemical redox potential of $U^{\circ}(\text{S}^{+}/\text{S}^{*})$ to a semiconductor $\mathbf{k}$ state at $\epsilon (= E - E_{\text{CB}})$ above the band edge (with flatband potential of U°_{CB}), the reaction can be written as



The driving force for this reaction is $\Delta G(\epsilon) = \Delta G_0 + \epsilon$, where the free-energy change for electron transfer to the band edge is $\Delta G_0 = -q[U^{\circ}_{\text{CB}} - U^{\circ}(\text{S}^{+}/\text{S}^{*})]$. The total ET rate from adsorbate to semiconductor becomes

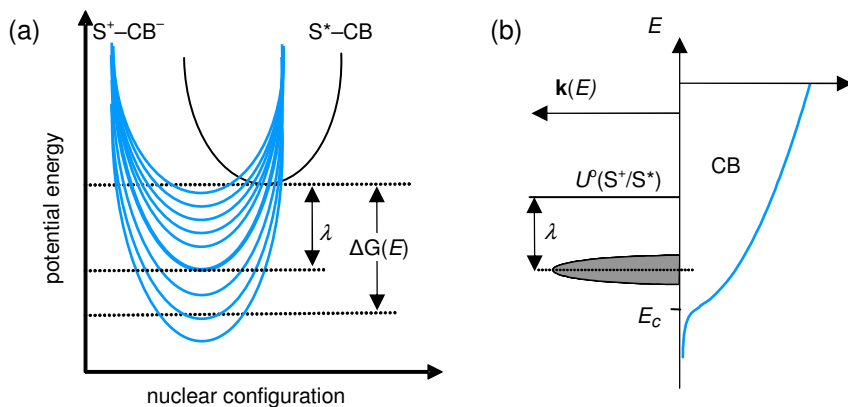


Figure 11.5 (a) Potential energy surface for electron transfer from a reactant state (S^*-CB) to a continuous manifold of product states (S^+-CB^-), corresponding to electrons in different $\mathbf{k}$ states in the semiconductor. The driving force $\Delta G(E)$ and barrier to ET vary with the energy of the $\mathbf{k}$ states, with barrierless ET (thick line) occurring to states at energy λ below the adsorbate potential; (b) Schematic illustration of variation of the density of semiconductor states with energy E . The electron-accepting states (shaded area) are determined by the adsorbate excited-state oxidation potential $U^\circ(S^+/S^*)$ and the reorganisation energy λ .

$$k_{ET} = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} d\varepsilon \rho(\varepsilon) (1 - f(\varepsilon, \varepsilon_F)) |\bar{H}(\varepsilon)|^2 \frac{1}{\sqrt{4\pi\lambda kT}} \exp\left[-\frac{(\lambda + \Delta G_0 + \varepsilon)^2}{4\lambda kT}\right] \quad (11.3)$$

where $\rho(\varepsilon)$ is the density of electron-accepting states at energy ε , which can include both bulk states and surface states, $H(\varepsilon)$ is the average electronic coupling between the adsorbate excited state and all $\mathbf{k}$ states in the semiconductor at the same energy ε , and λ is the total reorganisation energy. The Fermi occupancy factor $f(\varepsilon, \varepsilon_F)$ ensures that electron injection occurs only to unfilled states in the semiconductor. For undoped wide-bandgap semiconductors that are not under external bias, electron population in the conduction band is negligible.

It is informative to evaluate the trends in the ET rate using simple models of $H(\varepsilon)$ and $\rho(\varepsilon)$ that are likely to be qualitatively correct for many semiconductors. For metal oxides, the conduction-band states are composed primarily of empty orbitals of the metal ions, such as Ti^{4+} 3d orbitals in TiO_2 and Sn^{4+} 5s and 5p orbitals in SnO_2 (Henrich and Cox, 1996). Many adsorbates used for sensitisation are believed to bind with the metals ions via their anchoring groups such as $-PO_3H_2$ and $-COOH$ (Vittadini *et al.*, 2000). It is assumed that electronic interaction of adsorbate with the nanoparticle only involves the metal ions that are in direct contact with the anchoring

group with a total strength of H_0 . (The main picture will not change if the coupling is extended to the first few layers of metal ions.) It is often assumed that the electronic coupling of the adsorbate with semiconductor is independent of the energy of the $\mathbf{k}$ states over a small energy range (Anderson, 1961). It is further assumed that the density of electron-accepting states is given by the total DOS. In a nanoparticle with N metal centres, the total density-of-states should scale with N , while the square of electronic coupling strength per state should depend inversely on N (Sakata *et al.*, 1990)

$$\begin{aligned}\rho(\varepsilon)d\varepsilon &= N\rho_0(\varepsilon)d\varepsilon \\ |H(\varepsilon)|^2 &= \frac{1}{N}|H_0|^2\end{aligned}\quad (11.4)$$

where $\rho_0(\varepsilon)$ is the DOS per unit energy within the average volume V_0 of a metal centre, calculated by dividing the unit cell volume by the number of enclosed centres.

Under these assumptions, the total injection rate is independent of nanoparticle size for particles that are not in the quantum-confined regime, and can be expressed as

$$k_{\text{ET}} = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} d\varepsilon \rho_0(\varepsilon) |H_0|^2 \frac{1}{\sqrt{4\pi\lambda kT}} \exp\left[-\frac{(\lambda + \Delta G_0 + \varepsilon)^2}{4\lambda k_B T}\right] \quad (11.5)$$

It is assumed the DOS near the conduction-band edge in a perfect oxide crystal can be described by (Pankove, 1975)

$$\rho_{\text{oc}}(\varepsilon)d\varepsilon = V_0 \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^3} \sqrt{\varepsilon} d\varepsilon \quad (11.6)$$

where m^* is the effective mass of electrons in the conduction band. For most metal oxide nanocrystalline thin films, there exist an exponential tail of defect states below the band edge (Nelson, 1999; Nelson *et al.*, 2001). The existence of defects perturbs the energy of a perfect crystal and the perturbation is assumed to obey a gaussian distribution. A similar approach is often used to model amorphous semiconductors (Morigaki, 1999). The total DOS in nanocrystalline films can be modelled as

$$\rho_0(\varepsilon) = \int_0^{\infty} \rho_{\text{oc}}(\varepsilon') \frac{1}{\Delta\sqrt{2\pi}} e^{-\frac{(\varepsilon-\varepsilon')^2}{2\Delta^2}} d\varepsilon' \quad (11.7)$$

Inclusion of defects leads to negligible change of state density above the band edge, but creates substantial DOS below the band edge that decay roughly exponentially ($g(\varepsilon) \sim e^{\alpha\varepsilon}$). The decay rate α decreases as the width of the gaussian

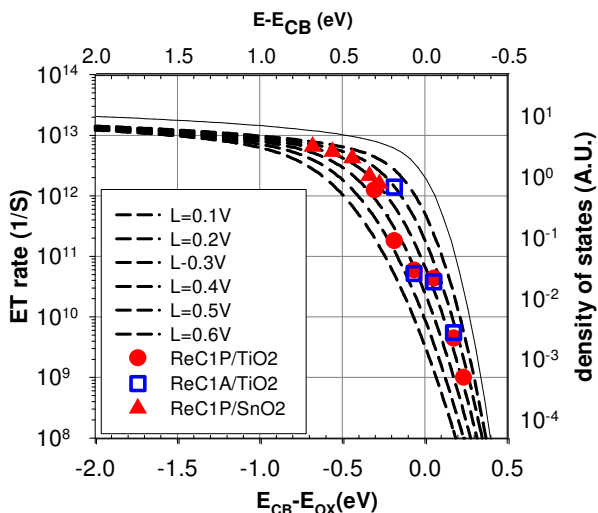


Figure 11.6 Comparison of calculated electron injection rate (dashed line) as a function of ΔG_0 and the measured electron injection rate (symbols) in ReC1A and ReC1P on TiO_2 and ReC1P on SnO_2 at different pHs. The calculated rates were obtained using eq. 11.5 for a range of reorganisation energies (0.1–0.6 eV) for anatase TiO_2 ($m^* = 10m_e$) with $H_0 = 100 \text{ cm}^{-1}$, which leads to the best agreement with the measured values for ReC1P/ TiO_2 . The measured injection rates for ReC1P/ SnO_2 and ReC1A/ TiO_2 have been multiplied by factors of 15 and 11, respectively, to allow comparison on the same curves. The thin solid curve shows a plot of the density-of-states in the semiconductor (right axis) as a function of energy relative to the band edge (top axis), calculated using eq. 11.7 with $\Delta = 100 \text{ meV}$. Reprinted with permission from *J. Phys. Chem. B* **109**, 19345 (2005). Copyright (2005) American Chemical Society.

distribution increases. Figure 11.6 shows a curve calculated for a gaussian distribution function of width Δ of 100 meV. The corresponding density of states decays roughly exponentially below the band edge with a decay constant of $\alpha = 15 \text{ (eV)}^{-1}$, similar to those used to model defect state densities of TiO_2 nanocrystalline electrodes in other studies (Nelson, 1999; Nelson *et al.*, 2001; Willis *et al.*, 2002; Nelson *et al.*, 2004).

The simple model described by eq. 11.5 should serve as a useful starting point to test non-adiabatic interfacial ET theory. The predicted dependence on electronic coupling, density of semiconductor states, adsorbate potential and reorganisation energy can be tested experimentally. As shown in Fig. 11.6, the calculated injection rate increases the further the adsorbate excited-state oxidation potential lies above the conduction band edge. The variation is slow ($\sim \epsilon^{1/2}$) high above the band edge, but nearly exponential near the band edge, reflecting the energy-dependent DOS in the semiconductor.

In the intermediate to strong coupling limit, interference of different reaction pathways with the continuum of accepting states in the semiconductor presents a non-trivial problem (Miller *et al.*, 1995; Gao *et al.*, 2000; Gao and Marcus 2000; Gosavi and Marcus, 2000). For electronically adiabatic interfacial electron transfer, formalisms based on the Anderson-News Hamiltonian are often used (Smith and Hynes, 1993; Miller *et al.*, 1995; Schmickler and Mohr, 2002 and references therein). The electronic coupling strength can influence the barrier height and therefore the rate. The injection rate can also be limited by the frequency of nuclear motion along the reaction coordinate, a notion that has been examined for adiabatic ET in molecular systems (Weaver *et al.*, 1990; Weaver, 1992; Barbara *et al.*, 1996).

11.3.2 Dependence on relative energetics

In inter- or intra-molecular electron transfer between two discrete donor and acceptor states, the ET rate depends on the driving force of electron transfer, exhibiting the normal, barrierless and inverted regimes (Marcus and Sutin, 1985). In interfacial ET, the total rate is a sum of rates of parallel ET processes to the continuum of states in the semiconductor, with driving forces spanning all three regimes. The dependence of ET rate on the relative energetics of the adsorbate excited state and conduction-band edge arises from the variation of the density of states with energy in the conduction band, as shown in Fig. 11.6. So far, three different approaches have been used to test the dependence of ET on the density of states.

The first method is to compare injection kinetics to the same semiconductor from adsorbates with different excited state potentials. As shown in Fig. 11.7, N3, 505 and 470 have the same pair of dcby ligands and differ only in the third pair of coordination ligands. This leads to lowering of the ground and excited-state oxidation potential from N3, as between 505 and 470. When comparing electron injection dynamics from these complexes, it is often observed that the fastest ET rate is observed in N3. This trend is similar on TiO_2 (Asbury *et al.*, 2003), SnO_2 (Asbury *et al.*, 2001a; Ai *et al.*, 2005), Nb_2O_5 (Ai *et al.*, 2004) and In_2O_3 (Guo *et al.*, 2006). The higher potential of the RuN3 excited states leads to injection to states at higher energy above the conduction-band edge, which for most semiconductors corresponds to a higher density of electron-accepting states. These comparisons provide strong evidence for the dependence of the ET rate on the density of states, although a quantitative test of the relationship is somewhat difficult because of the possibility of significant differences in electronic coupling strength among these adsorbates.

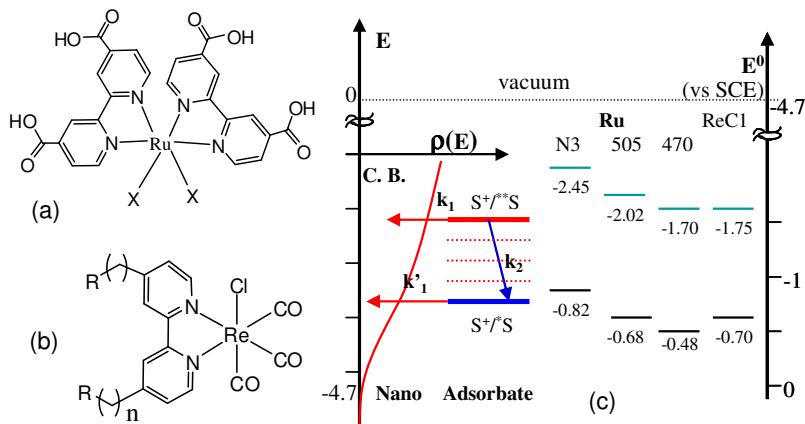


Figure 11.7 Structures of (a) $\text{Ru}(\text{dcbpy})_2(\text{X})_2$ [$2\text{X} = 2\text{NCS}^-$, CN^- and dcbpy , called N3 or Ru535, Ru505 and Ru470 respectively]; (b) $\text{Re}(\text{LCnR})(\text{CO})_3(\text{Cl})$ ($\text{LCnR} = 2\text{'-bipyridine-4,4'-(CH}_2)_n\text{-R}$, called ReCnA for $\text{R} = \text{COOH}$ and ReCnP for $\text{R} = \text{PO}_3\text{H}_2$). (c) Left panel: schematic illustration of two-state injection model, showing electron injection (rate constant k_1) from the unthermalised excited state S^{**} , intramolecular relaxation (k_2), and injection (k_1') from the relaxed excited state S^* . Right panel: redox potentials of the adsorbate non-relaxed and relaxed excited state (Asbury *et al.*, 2003). The potential for the $^1\text{MLCT}^*$ state is calculated for excitation at 400 nm (3.1 eV). Reproduced with permission from *J. Phys. Chem. B* **107**, 7376 (2003). Copyright 2003 American Chemical Society.

The second approach is to modify the conduction-band edge position, which can be tuned by pH or concentration of potential-determining ions (Finklea, 1988; Redmond and Fitzmaurice, 1993; Lyon and Hupp, 1999). It has been observed that the conduction band-edge position of metal oxides exhibits a nernstian type of dependence on the pH of the solution (Finklea, 1988; Enright *et al.*, 1994; Lyon and Hupp, 1999).

$$E_{\text{CB}}^0(\text{pH}) = E_{\text{CB}}^0(0) - 0.059V * \text{pH} \quad (11.8)$$

In addition to protons, other small cations (Li^+ , Na^+) have also been shown to affect band-edge positions in aprotic solvents, with the potential-determining ability related to the ability of the cations to intercalate into the semiconductor lattice (Redmond and Fitzmaurice, 1993).

There have been many reports of pH-dependent photocurrents (Watanabe *et al.*, 1976; Clark and Sutin, 1977; Sonntag and Spitler, 1985). Although injection rates were not directly measured in these early studies, their pH dependence has been suggested to be the main reason for observed change in photocurrent. In a recent study, electron injection rates from ReC1P (see Fig. 11.7) to TiO_2 and SnO_2 films at

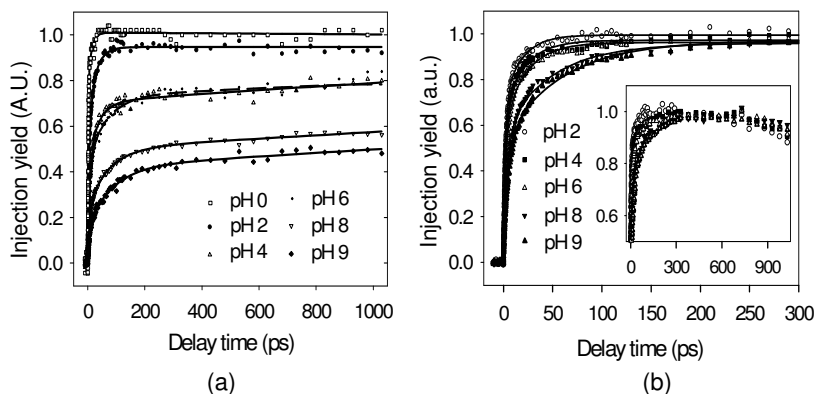


Figure 11.8 Comparison of the electron-injection kinetics for ReC1P on (a) TiO₂ films at pH 0–9; (b) SnO₂ films at pH 2–9 following excitation at 400 nm. The symbols are experimental data and the solid curves are best multi-exponential fits. Reproduced with permission from *J. Phys. Chem. B* **109**, 19345 (2005) (She *et al.*, 2005). Copyright 2005 American Chemical Society.

various pH were directly measured (She *et al.*, 2005). Shown in Fig. 11.8a is a comparison of the injection kinetics from ReC1P to TiO₂ at pH 0–9. The electron injection rate (characterised by the inverse of the half-rise time) decreases by about 1000-fold from pH 0 to 9. For the same adsorbate on SnO₂ (Fig. 11.8b), a much smaller pH dependence was observed (the half-rise time decreases by a factor of 4 between pH 2 and 9). The dramatically different dependence on these semiconductors was attributed to their different band-edge positions. For ReC1P on TiO₂, the adsorbate excited oxidation potential (~ -0.7 V vs. SCE) is very close to the band edge of TiO₂ (-0.4 to -0.94 V vs. SCE at pH = 0–9), and the electron-accepting states are near and below the band edge, whose density of states depends sensitively on energetics. For injection to SnO₂, whose band edge is at -0.12 to -0.54 V (SCE) at pH = 2–9, the electron-accepting states are higher above the band edge, at which the density of states changes much more slowly with energetics. Shown in Fig. 11.6 is a plot of the observed rates as a function of ΔG_0 for different pHs. The observed dependence agrees well with predictions based on eq. 11.5 for both SnO₂ and TiO₂.

In the above comparison, it is assumed that adsorbate oxidation potential and electronic coupling strength varies negligibly with pH. It should be noted that changing pH or cation concentration may also affect the adsorbate energetics and binding with the nanoparticle (Zaban *et al.*, 1998; Nazeeruddin *et al.*, 1999). The good agreement with the simple model shown in Fig. 11.6 suggests a dominating effect of band-edge change on the pH dependence of the interfacial ET rate. Similar pH-dependent ET rates were reported for N3 and 470 to TiO₂ (Asbury *et al.*, 2003).

Dependence of the injection rate on Li^+ concentration has also been reported (Tachibana *et al.*, 2001). Additionally, Meyer and coworkers observed a decrease of luminescence quantum yield at higher cation or proton concentration in Ru dye-sensitised TiO_2 film, suggesting similarly pH- and cation-dependent electron transfer rates (Kelly *et al.*, 1999; Qu and Meyer, 2001).

A third approach to control the density of accepting states is the application of an external bias to the photoelectrode (Iwai *et al.*, 2000; Tachibana *et al.*, 2001). Application of a more negative potential primarily raises the Fermi level in the conduction band, decreasing the density of unoccupied states. The injection rate from N3 to TiO_2 was found to decrease at more negative bias and the observed potential dependence was well fitted to a model similar to eq. 11.5 (Tachibana *et al.*, 2001). A similar retardation of injection rate with bias was also observed for $\text{Ru}(\text{bpy})_2(\text{dcbpy})$ on SnO_2 (Iwai *et al.*, 2000).

These observations confirm that the injection rate can be changed by changing the dye excited-state oxidation potential (comparing different dyes at the same pH), the conduction band-edge position (comparing the same dye at different pH or cation concentration), or the Fermi level in the semiconductor (via external bias). These three sets of measurements can all be understood by considering the change in density of electron-accepting states in the semiconductor, and suggest the dominating role of density of accepting states in determining the interfacial electron-transfer rate.

11.3.3 Dependence on electronic coupling

The strength of the electronic coupling between the molecular adsorbate and the semiconductor depends on the electronic structure of the donor molecule, the spacers and the anchoring group, and the semiconductor. One of the most convenient ways to vary the coupling strength systematically is to control the bridge length between the chromophore and the binding group. This approach was used successfully in earlier studies of thermal interfacial ET on metal or semiconductor electrodes modified by self-assembled-monolayers (SAM) of alkanethiols (Chidsey, 1991; Becka and Miller, 1992; Finklea and Hanshew, 1992; Smalley *et al.*, 1995; Sachs *et al.*, 1997; Gu and Waldeck, 1998; Creager *et al.*, 1999; Smalley *et al.*, 2003). Electron transfer mediated by longer bridges has generally been found to vary exponentially with the length of the bridge (Smalley *et al.*, 1995; Smalley *et al.*, 2003):

$$k_{\text{ET}}(r) = k_{\text{ET}}(r=0)e^{-\beta r} \quad (11.9)$$

where $k_{\text{ET}}(r=0)$ is the extrapolated rate constant for $r=0$, and β is the exponential decay constant. This dependence is attributed to an exponential decay of coupling strength with distance, which can be understood by the exponential dependence of the electron-tunnelling probability on distance or, more quantitatively, by a super-exchange model of transfer of electrons and holes through these bridges (Newton, 1991; Jordan and Paddon-Row, 1992).

The dependence at short bridge length is less well understood, and deviation from exponential dependence has been reported (Smalley *et al.*, 1995; Khoshtariya *et al.*, 2001; Sikes *et al.*, 2001; Smalley *et al.*, 2003). For photoinduced ET in dye-sensitised nanocrystalline thin films, only a few systematic studies of distance dependence have so far been reported. Distance-dependent electron injection processes to TiO_2 and SnO_2 were observed from a rhenium bipyridyl complex with $n=0-5$ methylene groups inserted between the bipyridine ligand and each of the two carboxylate binding groups, as shown in Fig. 11.7b (Asbury *et al.*, 2000; Anderson *et al.*, 2003a). On SnO_2 with $n \geq 3$ methylene bridges, the observed rate decreased exponentially with bridge length, with $\beta = \sim 1.0$ per methylene unit or $\sim 0.8 \text{ \AA}^{-1}$. The decay constant is similar to that observed for long methylene bridges (Smalley *et al.*, 1995; Smalley *et al.*, 2003). At shorter bridge lengths $n=2$ and $n=1$, similar injection rates ($\sim 1/40$ ps) were observed. The observed trend probably reflects the non-exponential dependence of coupling strength with distance at short chain lengths, which has been predicted in computational studies (Newton, 1991; Curtiss *et al.*, 1993; Liang and Newton, 1993). Other studies have reported weak distance dependence in ET through short bridges (Kilsa *et al.*, 2003; Piotrowiak *et al.*, 2003). In many studies, knowledge of the flexibility of the bridge and surface-binding modes is often lacking, which hinders a quantitative understanding of distance dependence.

In addition to the bridge, the anchoring group provides another control of electronic coupling strength in interfacial electron transfer. The most common anchoring groups for metal oxides are based on phosphonate, carboxylate, catechol and their derivatives (O'Regan and Grätzel, 1991; Heimer *et al.*, 1996; Gillaizeau-Gauthier *et al.*, 2001; Odobel *et al.*, 2003). The identity, number and location of the anchoring groups have been shown to affect photocurrent, suggesting their influence on charge separation and recombination kinetics (Heimer *et al.*, 2000; Hara *et al.*, 2002; Odobel *et al.*, 2003). Variation of the injection rate with the position of the anchoring group has been reported (Piotrowiak *et al.*, 2003). It was shown that the electron-injection rate from an ReCl complex (Fig. 11.7) to TiO_2 is significantly slower through carboxylate than through phosphonate anchoring groups (She *et al.*, 2005).

11.3.4 Ultrafast biphasic electron injection from N3 to TiO₂

Among numerous adsorbate/semiconductor combinations, the best solar-to-electric power conversion efficiency has been achieved in solar cells based on N3-sensitised TiO₂ nanocrystalline thin films (O'Regan and Grätzel, 1991; Nazeeruddin *et al.*, 1993). As a result, ET dynamics in this system have been most extensively studied (Tachibana *et al.*, 1996; Hannappel *et al.*, 1997; Ellingson *et al.*, 1998; Ellingson *et al.*, 1999; Asbury *et al.*, 1999a; Haque *et al.*, 2000; Heimer *et al.*, 2000; Tachibana *et al.*, 2001; Asbury *et al.*, 2001a; Asbury *et al.*, 2001b; Benko *et al.*, 2002; Kallonen *et al.*, 2002; Kuciauskas *et al.*, 2002; Asbury *et al.*, 2003). It is now generally accepted that the dynamics of photoinduced electron injection from N3 to TiO₂ are biphasic, consisting of a distinct <100 fs ultrafast component and one or more slower components on the picosecond and longer time scales.

The cause of the ultrafast electron injection from N3 and the mechanism of the biphasic injection has been a subject of considerable interest. This is discussed briefly here, and at greater length in Chapter 8. To help understand the injection dynamics, it is useful to review the photophysics of N3. Like many Ru bipyridyl complexes, the optical absorption spectrum of N3 is dominated by singlet metal-to-ligand-charge-transfer (¹MLCT) bands, which can be roughly considered as a transfer of electron density from the Ru T_{2g} *d* orbitals to the π^* orbital of the bipyridine. Recent DFT studies suggest that there is a strong mixing of the metal *d* orbital with SCN⁻ groups and the MLCT bands consists of transitions to a dense manifold of excited states (Monat *et al.*, 2002). Optical excitation of N3 with a visible photon excites the molecule to the ¹MLCT states, at ~1–2 eV above the lowest energy ³MLCT state, depending on the excitation photon energy (see Fig. 11.7). The excited molecules can undergo rapid electronic relaxation (internal conversion and intersystem crossing) within the excited state manifold to the ³MLCT states and concurrent vibrational energy redistribution and relaxation and solvation relaxation (Barbara and Jarzeba, 1990; Rosenthal *et al.*, 1991; Damrauer *et al.*, 1997; Castner and Maroncelli, 1998). The singlet-to-triplet intersystem crossing time has been determined to be ~75 fs for adsorbed N3 on TiO₂ in acetonitrile (Benko *et al.*, 2002; Kallonen *et al.*, 2002).

In the light of the rapid excited-state relaxation dynamics and the observed <100 fs electron injection component, the fast injection component must occur from non-equilibrated excited states. Distinct singlet and triplet electron-injection pathways have been observed for Ru polypyridyl complexes on SnO₂ (Iwai *et al.*, 2000) and TiO₂ (Benko *et al.*, 2002; Kallonen *et al.*, 2002). In a detailed study of electron injection dynamics in N3/TiO₂ (Benko *et al.*, 2002; Kallonen *et al.*, 2002), 55% of electron injection was shown to occur with ~50 fs injection time from singlet MLCT

states by monitoring the decay of the stimulated emission of the singlet states and the rise of absorption by the triplet and oxidised adsorbate. The remaining 50% of injection, on the 1–100 ps timescale, was confirmed to occur from the triplet state by recording the transient absorption spectra (extending from 400–1000 nm) of the triplet state, oxidised form and injected electrons, as shown in Fig. 11.3.

Further evidence of injection from unrelaxed excited states comes from excitation wavelength-dependent studies. Injection from the unrelaxed excited state must compete with intramolecular relaxation within the excited-state manifold. By varying the excitation wavelength, the molecules can be excited to different energy levels, affecting the branching ratio between the intramolecular relaxation and the interfacial electron-transfer pathways. Indeed, excitation wavelength dependence of injection dynamics has been reported (Benko *et al.*, 2002; Kallioinen *et al.*, 2002; Kuciauskas *et al.*, 2002; Asbury *et al.*, 2003; Anderson *et al.*, 2003b). Shown in Fig. 11.9 is a comparison of injection kinetics of Ru N3-sensitised TiO₂ films in a 1:1 ethylene/propylene carbonate mixture with excitation at 400, 530, and 630 nm (Asbury *et al.*, 2003). In this study, the IR absorption of injected electrons in TiO₂ was monitored. These kinetics traces, normalised to the same signal magnitude at 150 ps, consist of fast (<100 fs) and slow injection components (Asbury *et al.*, 2003). The amplitude of the fast injection component decreases at longer excitation wavelengths. In this case,

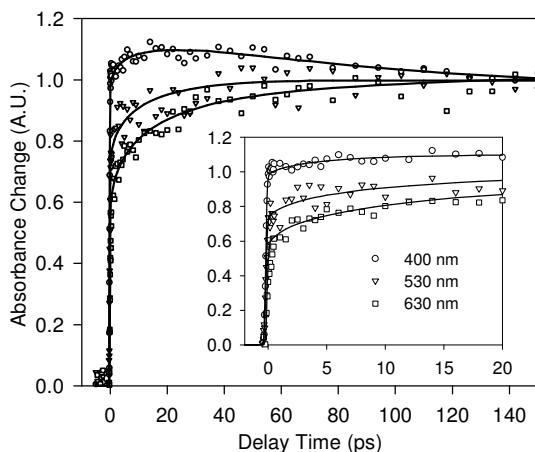


Figure 11.9 Normalised comparison of electron absorption dynamics of N3-sensitised TiO₂ films in ethylene/propylene carbonates (1:1) following excitation at different wavelengths. Inset: the same data plotted on a shorter time scale. The solid lines are fits using the two-state injection model. The fast component is well described by a <100 fs rise and the slow component is fitted by a stretched exponential function with a 50 ps time constant. Reproduced with permission from *J. Phys. Chem. B* **107**, 7376 (2003) (Asbury *et al.*, 2003). Copyright 2003 American Chemical Society.

the instrument response function (~150 fs) was not short enough to resolve the difference in the rate of fast components. With better time resolution, this difference can be directly resolved (Benko *et al.*, 2002; Kalloinen *et al.*, 2002). Excitation wavelength-dependent injection kinetics were also observed in N3-sensitised ZnO (Anderson *et al.*, 2003b) and SnO₂ (Ai *et al.*, 2005; Guo *et al.*, 2006). (Iwai *et al.*, 2000; Benko *et al.*, 2003a; Ai *et al.*, 2005); ZnO (Asbury *et al.*, 1999b; Furube *et al.*, 2003; Anderson *et al.*, 2003b) and Nb₂O₅ (Ai *et al.*, 2004).

11.3.5 Dependence on the semiconductor

In addition to TiO₂, there is also considerable interest in dye-sensitised solar cells based on other metal oxides, such as ZnO (Rensmo *et al.*, 1997; Sayama *et al.*, 1998; Hara *et al.*, 2000), Nb₂O₅ (Hu *et al.*, 1995; Barros Filho *et al.*, 1997; Sayama *et al.*, 1998; Hara *et al.*, 2000; Aegerter, 2001; Lenzenmann *et al.*, 2001; Aegerter *et al.*, 2002), SnO₂ (Bedja *et al.*, 1994; Ferrere *et al.*, 1997; Hara *et al.*, 2000), WO₃ (Sayama *et al.*, 1998), Ta₂O₅ (Sayama *et al.*, 1998) and In₂O₃ (Sayama *et al.*, 1998; Hara *et al.*, 2000). However, so far the reported conversion efficiencies are significantly lower than those based on N3-sensitised TiO₂ (Nazeeruddin *et al.*, 1993). The reasons for these lower conversion efficiencies remain unclear. It is therefore important to compare electron injection and recombination kinetics in different semiconductors and to understand their dependence on the properties of the semiconductor.

There have been numerous studies of electron injection from various adsorbates into TiO₂, many of which reported <100 fs electron-injection components (Rehm *et al.*, 1996; Tachibana *et al.*, 1996; Cherepy *et al.*, 1997; Hannappel *et al.*, 1997; Ellingson *et al.*, 1998; Ghosh *et al.*, 1998a; Ellingson *et al.*, 1999; Martini *et al.*, 1999; Asbury *et al.*, 1999a; Haque *et al.*, 2000; Heimer *et al.*, 2000; Tachibana *et al.*, 2001; Zimmermann *et al.*, 2001; Asbury *et al.*, 2001a; Asbury *et al.*, 2001b; Benko *et al.*, 2002; Huber *et al.*, 2002; Kalloinen *et al.*, 2002; Kuciauskas *et al.*, 2002; Asbury *et al.*, 2003). Although much less extensively studied, electron-injection dynamics to other metal oxide semiconductors, such as SnO₂ (Iwai *et al.*, 2000; Asbury *et al.*, 2001a; Bauer *et al.*, 2002; Benko *et al.*, 2003a; Ai *et al.*, 2005), ZnO (Asbury *et al.*, 1999b; Bauer *et al.*, 2001; Furube *et al.*, 2003; Anderson *et al.*, 2003b), Nb₂O₅ (Ai *et al.*, 2004) and In₂O₃ (Guo *et al.*, 2006) have also been examined. Comparison of ET to different semiconductors should take into account the differences in the conduction-band electronic structures and band-edge positions. These differences affect the electronic coupling strength with the adsorbate and the electron-accepting state density in the conduction band, both of which change the ET rate. Furthermore,

since injection dynamics depend on the properties of both the adsorbates and the semiconductors, to investigate their dependence on the semiconductor, it is helpful to compare kinetics involving the same adsorbate. Unfortunately, only a few systematic studies have been designed for this type of comparison. Therefore, instead of a comprehensive review of all published works on different semiconductors, the remainder of this section is focused on one set of studies that compare electron injection dynamics from N3 to different semiconductors.

In a recent series of studies, the injection dynamics of N3, 505 and 470 to TiO_2 , Nb_2O_5 , SnO_2 , ZnO and In_2O_3 were compared (Asbury *et al.*, 1999a; Asbury *et al.*, 1999b; Asbury *et al.*, 2003; Anderson *et al.*, 2003b; Ai *et al.*, 2004; Ai *et al.*, 2005; Guo *et al.*, 2006). Shown in Fig. 11.10a is the comparison of injection dynamics from N3 to TiO_2 , Nb_2O_5 , ZnO and SnO_2 films (exposed to air), measured at 400 nm excitation (Asbury *et al.*, 1999a; Asbury *et al.*, 2001a; Asbury *et al.*, 2003; Anderson *et al.*, 2003b; Ai *et al.*, 2004; Ai *et al.*, 2005). Injection kinetics to all semiconductors are biphasic, but the amplitude of the fast component varies significantly. The amplitude of the fast component is much larger in TiO_2 and Nb_2O_5 than in ZnO and SnO_2 . Figure 11.10b shows a comparison of injection kinetics from N3 to SnO_2 and In_2O_3 measured with 530 nm excitation. The kinetics of injection to these semiconductors are similar.

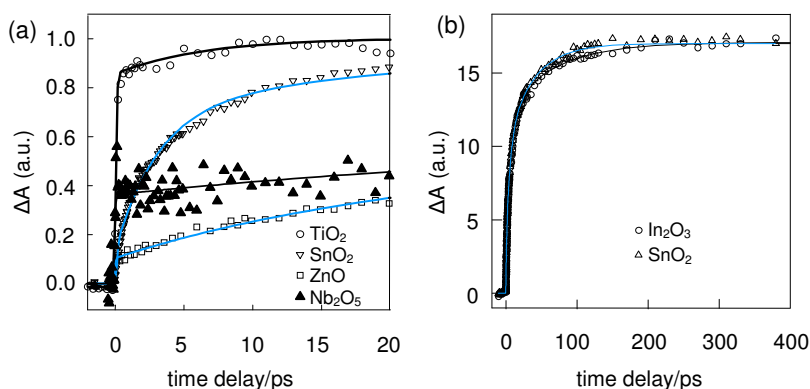


Figure 11.10 (a) Comparison of electron-injection kinetics from N3 to TiO_2 (open circles), SnO_2 (open triangles), ZnO (open squares) and Nb_2O_5 (filled circles) films (exposed to air) following 400 nm excitation; (b) Comparison of electron-injection kinetics from N3 to In_2O_3 (circles) and SnO_2 (triangles) thin films (in pH2 buffer) following 530 nm excitation.

As we have already noted, the biphasic injection kinetics suggest that the fast and slow injection components relate to injection into different sets of states in the semiconductor and should be compared separately. The fast injection component involves states high above the band edge. According to the two-state injection model, (see eq. 11.8), the rise time of the fast component, $1/(k_1 + k_2)$, is <75 fs for N3 on all semiconductors ($k_2 = 1/75$ fs) (Benko *et al.*, 2002; Kallonen *et al.*, 2002) and its difference is not well-resolved in our measurements, which had >100 fs time resolution. However, the difference in their relative amplitudes, given by $k_1/(k_1 + k_2)$, suggests the k_1 trend $\text{TiO}_2 > \text{Nb}_2\text{O}_5 \gg \text{SnO}_2 \sim \text{ZnO}$. The slow injection component originates from the relaxed $^3\text{MLCT}$ states and injection into TiO_2 , Nb_2O_5 and ZnO probably involves states near and below the band edge. The density of states in this region has been shown to depend critically on such sample conditions as sintering temperature, pH and solvent environment (Asbury *et al.*, 1999a; Asbury *et al.*, 2003; Anderson *et al.*, 2003b; Benko *et al.*, 2003b; Ai *et al.*, 2004; Ai *et al.*, 2005; She *et al.*, 2005). The comparison of the slow injection components in these samples will be strongly affected by experimental conditions, and does not reflect the dependence on the intrinsic properties of the different semiconductors. For N3 on SnO_2 and In_2O_3 , because of the ~ 0.5 V lower conduction-band edge in these systems (compared with TiO_2), injection from the relaxed excited state is still significantly above the band edge, rendering a meaningful comparison possible. As shown in Fig. 11.10b the injection kinetics from N3 to SnO_2 and In_2O_3 (in pH2 buffer following 532 nm excitation) are dominated by the slow injection component, suggesting that the injection rate from relaxed $^3\text{MLCT}$ states to these semiconductors is similar.

The conduction-band edge positions of TiO_2 and ZnO are similar, but ~ 0.5 eV lower in SnO_2 and In_2O_3 , and ~ 0.2 eV higher in Nb_2O_5 (Hagfeldt and Grätzel, 1995). There is no obvious correlation of rate with band-edge position. The conduction bands of TiO_2 and Nb_2O_5 are mainly comprised of empty d orbitals of Ti^{4+} and Nb^{5+} , respectively, while those of ZnO , SnO_2 and In_2O_3 are mainly empty s and p orbitals of Zn^{2+} , Sn^{4+} and In^{3+} , respectively (Henrich and Cox, 1996). Typically d bands are narrower and their densities-of-states are orders of magnitude higher than those of sp bands (Pankove, 1975; Henrich and Cox, 1996). It has been hypothesised that the trend in ET rate (or amplitude) of the fast component may be caused mostly by the differences in the density of states in d - vs. sp -type conduction bands (Anderson and Lian, 2005b). For the same reason, the similar injection rate from the relaxed $^3\text{MLCT}$ state of N3 to SnO_2 and In_2O_3 may be a reflection of the similar conduction-band state density in these materials (Guo *et al.*, 2006).

11.4 Summary

Electron injection in many dye-sensitised metal oxides can occur on the ultrafast time scale. This process has been extensively studied in recent years because of its important role in determining solar cell performance. Among the many available ultrafast techniques, transient absorption in the visible and mid-IR are the most commonly used because of their ability to monitor both the reactants and products of ET on the ultrafast time scale. From extensive studies by many groups, a qualitative understanding of interfacial electron-injection dynamics from adsorbate molecules to semiconductors has emerged. It is useful to view the adsorbate/semiconductor system as a donor–bridge–acceptor complex and to design experiments to test the dependence of the ET rate on the various components of the system systematically. There is a continuum of electron-accepting states in the semiconductor conduction band, and the interfacial ET rate depends on the density of accepting states in the semiconductor. This dependence was experimentally demonstrated by changing the relative energetics between the adsorbate excited state and the conduction band edge through changing the adsorbate potential, the band-edge position or the Fermi level. The dependence of the injection rate on the electronic coupling strength has been demonstrated by varying the length of spacer groups between adsorbate and semiconductor, and by changing the anchoring group. For ruthenium polypyridyl complexes adsorbed on metal oxides, the injection kinetics are typically biphasic, consisting of both ultrafast (<100 fs) and slower injection components. These components are attributed to injection from unrelaxed and relaxed excited states, respectively, and their relative amplitudes are determined by the ratio of the rates of injection and intramolecular relaxation from the unrelaxed state. Comparison of injection dynamics from N3 to different metal oxides suggests a dominating effect of density of conduction band states in determining interfacial electron transfer rates.

Much experimental progress will be needed to achieve more quantitative understanding of interfacial ET dynamics. Most injection kinetics are highly non-single exponential, reflecting a broad inhomogeneous distribution. New experimental techniques, such as single-molecule fluorescence spectroscopy, are needed to probe the origins of these distributions more sensitively. The inhomogeneity may in part arise from a distribution of surfaces and defects present in nanomaterials. Comparison with similar measurements on well-characterised single-crystal surfaces will assist better understanding. This requires surface-selective time-resolved techniques such as second-harmonic generation and sum-frequency generation. These approaches can also be used to determine the adsorption geometry of adsorbates on the surface, knowledge of which will be important for comparison with theoretical studies.

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CHAPTER 12

EXPERIMENTAL TECHNIQUES IN PHOTOELECTROCHEMISTRY

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Give me the splendid silent sun with all his beams full-dazzling.

Walt Whitman, Give Me the Splendid Silent Sun, 1900

12.1 Introduction

Photoelectrochemistry is an interdisciplinary subject that brings together different aspects of solid-state physics, electronics and chemistry. This interdisciplinarity, which is part of the fascination of photoelectrochemistry, is reflected in the unusually wide range of techniques employed to characterise photoelectrochemical systems. The objective of this chapter is to provide an overview of these techniques and to illustrate their application to practical systems.

Since parallels exist between semiconductor/electrolyte junctions and solid-state analogues, many experimental techniques for the study of photoelectrochemical systems have been introduced from semiconductor physics and technology. However, it is important to realise that chemical and electrochemical reactions can occur at semiconductor/liquid interfaces, limiting the extent to which theory and interpretation can be borrowed from solid-state physics: see Schroder (1998) for a comprehensive review of methods for semiconductor materials and device characterisation and McHardy *et al.* (1992) for technological aspects of semiconductor electrochemistry. Photoelectrochemical systems may also have unique properties that require new theoretical and experimental approaches. For example, the solid/liquid junction formed in porous nanocrystalline electrodes exhibits unusual properties that arise from the high internal surface area and the effective shielding of electronic charge by

the electrical double layer. The traditional semiconductor junction model is not applicable to these composite materials (Peter, 2007).

A number of spectroscopic techniques, as well as many of the tools of surface science, are used to study photoelectrochemical systems. The objective may be to monitor changes in the structure or chemical composition of the surface. Alternatively, the aim may be to probe the bulk properties of the semiconductor. Modulation techniques are particularly important, since they greatly enhance the sensitivity of spectroscopic measurements. It is not possible to give an exhaustive survey of all these methods in this chapter. Instead, we will emphasise the complementary nature of different techniques and the way that they can be used to achieve a deeper understanding of the physical and chemical processes taking place in photoelectrochemical systems. The reader is referred to a number of reviews and textbooks for a more detailed account of fundamental aspects of semiconductor electrochemistry (Morrison, 1980; Pleskov and Gurevich, 1986; Hamnett, 1987; Finklea, 1988; Sato, 1998; Peter, 1999; Memming, 2001).

12.2 Electrical methods

12.2.1 Single-frequency admittance measurements (*Mott–Schottky plots*)

Solid-state semiconductor junctions are commonly characterised by AC and DC electrical techniques. In the case of Schottky barrier (metal/semiconductor) devices, single admittance measurements (' C – V measurements') are often used to determine the space-charge layer capacitance C_{scl} as a function of applied voltage bias V . Analysis of the potential dependence of C_{scl} provides values of the barrier height and doping density. This method has been applied widely in semiconductor electrochemistry to determine flatband potentials and doping densities (Morrison, 1980). The semiconductor may be in contact with either a redox electrolyte or an inert supporting electrolyte. In the first case, the analogy with the metal/semiconductor junction is exact. The redox potential defines the Fermi energy (work function) of the contact, and hence the equilibrium barrier height. In the absence of redox species, the contact is essentially blocking, and the band bending is controlled by the externally applied voltage (ideally polarisable case).

Under depletion conditions, the withdrawal of majority carriers from the interfacial region of the semiconductor/electrolyte junction creates a space-charge layer consisting of ionised donors (for n -type semiconductors) or acceptors (for p -type semiconductors). The dependence of the space-charge density Q_{scl} on the potential

difference $\Delta\phi_{\text{sc1}}$ across the space-charge region defines the differential space-charge capacitance $C_{\text{sc1}} = \partial Q_{\text{sc1}} / \partial \Delta\phi_{\text{sc1}}$. If the doping density is less than 10^{18} cm^{-3} , and provided that no charge is stored in defects (surface states) at the semiconductor surface, changes in applied potential appear almost entirely across the space-charge region. Consequently, the potential drop in the Helmholtz layer at the interface remains almost constant. In this situation, $\Delta\phi_{\text{sc1}}$ is equal to $U - U_{\text{fb}}$, where U is the electrode potential (vs. a suitable reference electrode) and U_{fb} is the flatband potential. The capacitance under depletion and accumulation conditions is obtained by solving the Poisson–Boltzmann equation (details may be found in, for example, Morrison, 1980). Only the depletion case is considered here. The potential dependence of C_{sc1} is described by the Mott–Schottky equation (given here for an n -type semiconductor)

$$\frac{1}{C_{\text{sc1}}^2} = \frac{2}{qN_{\text{D}}\epsilon\epsilon_0} \left(U - U_{\text{fb}} - \frac{kT}{q} \right) \quad (12.1)$$

where N_{D} is the donor density and $\epsilon\epsilon_0$ is the permittivity of the semiconductor. Mott–Schottky plots of $1/C_{\text{sc1}}^2$ vs. U are used to obtain doping densities and flatband potentials. Since C_{sc1} is a potential-dependent differential capacitance, it must be measured using small-amplitude AC methods.

The ideal semiconductor/electrolyte interface forms a blocking junction under reverse-bias conditions, so the reverse-bias current density i_{Dk} is small and independent of voltage. For large-bandgap materials, reverse-bias currents are usually higher than predicted because surface defects allow some interfacial electron transfer to occur. The small-amplitude electrical behaviour of the junction is therefore represented by a parallel combination of the space-charge capacitance C_{sc1} and a resistance defined by $R_p = \partial U / \partial i_{\text{Dk}}$. The finite resistances of the ohmic contact and the solution also affect the AC response. These resistances are lumped into a single series resistance R_s to give the equivalent circuit shown in Fig. 12.1. Note that the Helmholtz capacitance C_{H} does not appear in the figure since in most cases C_{sc1} is much smaller than C_{H} (unless the semiconductor is highly doped), so that C_{H} (which

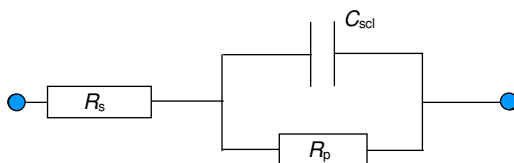


Figure 12.1 Simplest small-signal equivalent circuit representing the semiconductor/electrolyte junction under depletion conditions. R_s = total series resistance, R_p = parallel resistance due to charge transfer, C_{sc1} = space-charge layer capacitance.

appears in series with C_{scl}) can be neglected. A note of caution is appropriate here. If C_{H} is included for the case of highly-doped semiconductors, the inequality $C_{\text{scl}} \ll C_{\text{H}}$ is no longer valid, and the DC potential distribution must be obtained by solving the Poisson–Boltzmann equation with appropriate boundary conditions (Morrison, 1980).

If R_{s} is small and the applied electrical AC frequency f is chosen such that R_{p} is much greater than $1/2\pi f C_{\text{scl}}$, the impedance Z of the junction is dominated by C_{scl} , *i.e.* $Z \approx 1/j\omega C_{\text{scl}}$, where $\omega = 2\pi f$. Under these conditions, the admittance $Y = 1/Z = j\omega C_{\text{scl}}$. The magnitude of the admittance is therefore a linear function of C_{scl} , and its phase is $+90^\circ$. If R_{p} is comparable with $1/\omega C_{\text{scl}}$ (as is often the case at high frequencies), the out-of-phase (90°) component of the admittance is still given by $j\omega C_{\text{scl}}$, and the in-phase (0°) component is equal to R_{p}^{-1} . This approximation has been widely used as the basis for single-frequency measurements of C_{scl} as a function of potential, using the set-up shown in Fig. 12.2. A small-amplitude (≤ 10 mV) sinusoidal AC voltage is superimposed on the DC potential applied to the sample by the potentiostat. Since the AC current depends linearly on the admittance, the out-of-phase signal measured by the lock-in amplifier is a linear function of C_{scl} . The phase and sensitivity of the measurement system can be set using a set of calibrated capacitances in the appropriate range. The calibration should be repeated for each frequency.

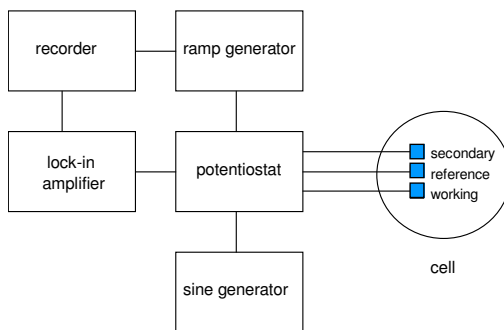


Figure 12.2 Experimental arrangement for single-frequency admittance (capacitance) measurements.

There are two main sources of error in this type of measurement. The first arises from the failure of the approximation $Y \approx j\omega C_{\text{scl}}$ if the sample has a poor ohmic contact or the frequency is too high. If this is the case, the out-of-phase component is no longer a linear function of C_{scl} . The error, which usually manifests itself as an unexpected frequency dependence of C_{scl} , can be avoided by making frequency-dependent impedance measurements with a frequency response analyser (as discussed in Section 12.2.2). The other source of errors arises from the frequency response of

the potentiostat circuit. In general, the AC voltage applied to the electrode is not identical with the signal used to programme the potentiostat. Its magnitude and phase are changed as a result of attenuation arising from the frequency response characteristics of the potentiostat circuit (including the electrochemical cell). The voltage output from the current-measuring amplifier is also attenuated and phase-shifted. The higher the measurement frequency, the more acute these problems become.

The simplest way around these problems is to set up the system with a calibrated capacitance box and a small ($<10\ \Omega$) series resistance to ensure potentiostat stability. The in-phase response is set accurately to zero by adjusting the phase control on the lock-in. The magnitude of the out-of-phase (90°) response is then calibrated over the range of interest using the capacitance box. The current amplifier should be set to a low sensitivity range to enhance the frequency response of the system: the output from the potentiostat to the lock-in should ideally be only a few millivolts, so that the current amplifier is operating in its small-signal regime.

Often the slopes and intercepts of Mott–Schottky plots are not independent of frequency, calling into question the validity of the simple approach outlined above. The simplest reasons for non-ideal Mott–Schottky plots are instrumental error or incorrect assumptions about the equivalent circuit. However, these plots are often not linear even in the absence of these artefacts. Physical explanations of non-linearity include non-uniform doping, surface roughness, surface states and deep donor or acceptor levels (Bonham and Orazem, 1992). In the case of thin semiconductor films, Mott–Schottky plots may reach a plateau at large values of $U - U_{fb}$, when the space charge extends throughout the film and C_{sc} tends towards the geometric capacitance $C_{geo} = d\epsilon\epsilon_0$, where d is the film thickness (Özsan *et al.*, 1996). Figure 12.3 illustrates this behaviour. The transition voltage V_{TR} can be used to find the film thickness.

Frequency dispersion can arise from dielectric relaxation, surface roughness, carrier trapping in the space-charge region and relaxation of deep donor/acceptor levels (Oskam *et al.*, 1991). One of the commonest causes of non-ideality in semiconductor/electrolyte junctions is the presence of states at the surface that can exchange electrons with the solid and liquid phases. These are referred to by the general term ‘surface states’, adopted from solid-state physics, but in most cases their structural and chemical identity is obscure. Even for a perfect solid/vacuum interface, termination of the lattice leads to energy states that lie in the bandgap, and surface reconstruction is common. Solid/liquid interfaces are more complex since atoms in the solid can form bonds with species from the solvent or electrolyte. This termination does not necessarily lead to surface states. In the case of silicon in fluoride media, for example, the surface is terminated by hydrogen atoms and the density of surface states is very low (Oskam *et al.*, 1996a, 1996b, 1996c; Hoffmann *et al.*, 1998). Oxide-

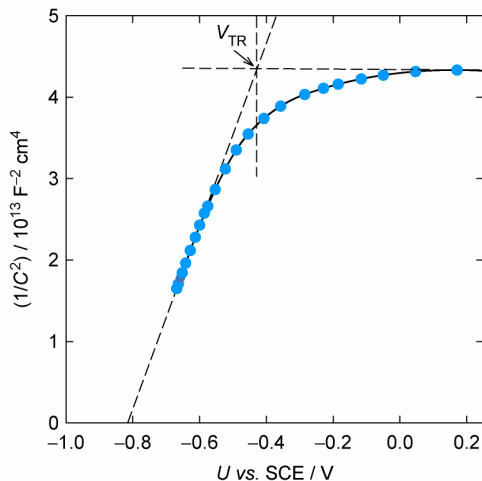


Figure 12.3 Mott-Schottky plot for a thin (80 nm) film of *n*-CdS on tin oxide-coated conducting glass, showing the transition from Mott-Schottky behaviour to the geometric capacitance limit when the space-charge region extends to the substrate. Electrolyte 0.1 mol dm⁻³ Na₂S, pH 13. Adapted from Özsan *et al.* (1996).

covered silicon surfaces, by contrast, are usually less ideal owing to the presence of sub-stoichiometric silicon compounds.

In an ideal semiconductor/electrolyte junction, the space charge in the semiconductor is balanced by the counter-charge in the electrical double layer formed in the electrolyte. Since the Helmholtz capacitance C_H is generally much larger than C_{sc} , most of the potential drop is located in the semiconductor. The surface ionic charge on the semiconductor is determined by the acid/base or ion-exchange properties of the surface. Oxide electrodes usually exhibit a Nernstian pH dependence of the flatband potential as a consequence of the change in surface dipole. However, high densities of electronic surface states can effectively 'metallise' the semiconductor surface. The surface charge then varies with applied potential in such a way that a significant fraction of the change in total potential difference appears across the Helmholtz double layer rather than across the space-charge region of the semiconductor. This effect is referred to as 'Fermi-level pinning' (Gilman *et al.*, 1993; Lewerenz, 1993; Hutton *et al.*, 1994). The surface states responsible for this effect may arise from crystal imperfections and surface damage, or they may be formed as a consequence of surface reactions, either in the dark or under illumination (Peter *et al.*, 1997). The effect of Fermi level pinning is manifest as a flat region in Mott-Schottky plots arising from the almost constant value of the total capacitance.

A special case of non-ideal Mott–Schottky behaviour arises if impurity atoms such as hydrogen diffuse into the near-surface region of the sample: this has been observed for *p*-GaP (Li *et al.*, 1984) and *p*-Si (Mandal *et al.*, 1990), where hydrogen atoms can act as ‘near-surface’ states, or compensate the doping, leading to an insulating surface region or even to conversion from *p*-type to *n*-type. This leads to large shifts in the apparent flatband potential.

12.2.2 Electrochemical impedance spectroscopy (EIS)

Many of the problems of interpretation that arise from single-frequency admittance measurements can be avoided if frequency-resolved measurements are made (Gomes and Vanmaekelbergh, 1996; Macdonald *et al.*, 1998). These can be carried out with a programmable lock-in amplifier or using a frequency response analyser (FRA) with its associated electrochemical interface. FRA systems are optimised to overcome the problems associated with attenuation and phase shift. The current to the cell is measured using a series resistance and a wide-bandwidth voltage amplifier, and the AC voltage appearing across the cell between the working and reference electrodes is measured directly to avoid errors arising from the performance of the potentiostat control amplifier. Provided that adequate care is taken, measurements can be extended into the MHz region.

In three-electrode measurements, the main source of error at high frequencies is the reference electrode. It is advisable to use a low-impedance reference electrode or a quasi-reference electrode such as an annealed Pt wire when making EIS measurements above 100 kHz. Lead lengths should be kept to a minimum to minimise stray inductance and capacitance, and the cell design should be optimised to minimise series resistance losses: glass frits used to separate the counter-electrode compartment are a common source of high-frequency artefacts, and these should be avoided.

FRA systems are versatile, and they can be controlled to acquire and analyse the data required to construct Mott–Schottky plots, for example. Unfortunately, the ease of use of FRA-fitting software can lead to errors of interpretation that arise from a failure to relate fitting elements to the physical system. Several equivalent circuits may give the same frequency-dependent impedance response. No *a priori* distinction between degenerate circuits is possible. It is necessary to study the system response as a function of additional experimental variables (DC voltage, concentration, mass transport conditions *etc.*) in order to establish whether the circuit elements are related in a predictable way to a model of the physical system.

EIS has been used to study the kinetics of outer-sphere redox reactions at semiconductors in the dark (Meier *et al.*, 1997; Meier *et al.*, 1999). The reactions involve majority carriers (electrons for n-type materials), and the electrode behaves like a metal with a low and potential-dependent electron density. The EIS response can be modelled by the equivalent circuit shown in Fig. 12.1, where R_p is interpreted as the faradaic resistance obtained by linearising the potential dependence of the current associated with electron transfer to the redox species.

EIS has also been used to study the dissolution of *p*-type silicon in fluoride media (Ozanam *et al.*, 1992; Bailes *et al.*, 1998). The system is interesting because the current–voltage curve exhibits a region of negative slope in the electro-polishing region, as shown in Fig. 12.4. Figure 12.5 shows examples of the impedance response. The high-frequency capacitance is associated with the presence of an oxide layer on the silicon. The low-frequency semicircle arises from the dissolution process. It can have a negative low-frequency intercept because R_p is the inverse of the slope of the steady-state current–voltage characteristic, which can be positive or negative. The parallel capacitance in this case is not C_{sc} , but a pseudocapacitance associated with the growth and dissolution of the surface oxide.

EIS measurements can also be carried out under conditions where illumination of the semiconductor generates a photocurrent. The technique is then referred to as photoelectrochemical impedance spectroscopy, PEIS. Interpretation of the results in terms of passive *RC* circuit elements is no longer appropriate since the system contains a current source. A more satisfactory approach is to relate the impedance response directly to the physical processes responsible for the photocurrent (Ponomarev and Peter, 1995; Peter, 1999; Peter and Vanmaekelbergh, 1999).

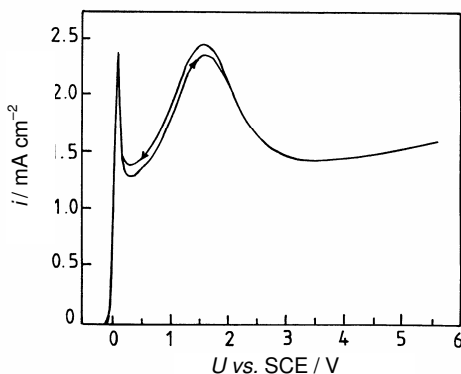


Figure 12.4 Steady-state current–voltage curve for *p*-Si(100) in 0.1 mol dm⁻³ NH₄F, pH 3. Note the change in slope from positive to negative at around 1.5 V. Adapted from Bailes *et al.* (1998).

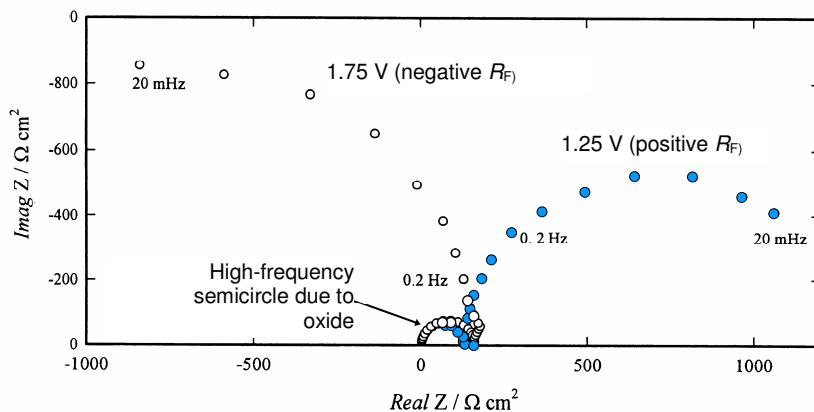


Figure 12.5 Complex-plane impedance plots for *p*-Si in 1.0 mol dm⁻³ NH₄F (pH 4.5). Note that the faradaic resistance R_F (derived from the low-frequency intercept on the real axis) can be positive or negative. The negative R_F value at 1.75 V indicates that the current decreases with increasing potential in this region of the current–potential curve (see Fig. 12.4). Adapted from Bailes *et al.* (1998).

12.3 Photocurrent, photovoltage and microwave reflectance methods

12.3.1 Photocurrent spectroscopy

When a semiconductor/electrolyte junction is illuminated, electrons can be excited from the valence band to the conduction band provided that the photon energy $h\nu$ exceeds the bandgap energy E_g . In addition, photons with lower energies may excite electrons or holes from surface or bulk traps to the bands, giving a sub-bandgap photoresponse. Under depletion conditions, minority carriers (holes in *n*-type and electrons in *p*-type semiconductors) created by light absorption in the space-charge region are transported rapidly ($<10^{-9}$ s) to the interface by drift/diffusion. Minority carriers generated deeper in the semiconductor may still be collected by diffusing to the edge of the space-charge region, or they may recombine with majority carriers at a rate that determines the bulk minority-carrier lifetime τ . Minority carriers reaching the surface either transfer across the interface in a photoelectrochemical reaction or recombine with majority carriers via surface states. The competition between these processes determines the fraction of photogenerated minority carriers that gives rise to the externally measured photocurrent. This fraction is the internal quantum efficiency.

Photocurrent spectroscopy involves quantitative measurement of the ratio of the electron flux in the external circuit to the incident photon flux (in some cases

corrected for reflection losses). IPCE is an accepted acronym for the corresponding incident photon-to-current conversion efficiency. The photocurrent response of an ideal semiconductor/electrolyte junction under reverse bias conditions with fast electron-transfer kinetics is described by the Gärtner equation (Gärtner, 1959)

$$\text{IPCE} = \frac{i_{\text{photo}}}{qj_0} = 1 - \frac{e^{-\alpha W}}{1 + \alpha L} \quad (12.2)$$

where j_0 is the incident photon flux (corrected for any reflection losses), α is the absorption coefficient, W is the width of the space-charge region and L is the minority-carrier diffusion length, the latter two being defined by the expressions

$$W = \left(\frac{2\epsilon\epsilon_0\Delta\phi_{\text{scl}}}{qN_d} \right)^{1/2} \quad (12.3)$$

$$L = (D\tau)^{1/2} \quad (12.4)$$

where N_d is the dopant density, D is the diffusion coefficient of minority carriers and τ is the minority-carrier lifetime in the bulk.

Figure 12.6 shows the usual set-up for photocurrent spectroscopy. A high-pressure xenon lamp is most convenient for UV/visible work. The incident wavelength is selected by a grating monochromator, and appropriate filters are used to remove harmonic components at 2λ and $\lambda/2$. The incident light intensity is generally low, so that photodecomposition reactions and thermal effects are minimised. The mechanical chopper interrupts the light periodically in order to allow a lock-in amplifier to be used to distinguish small photocurrents from background (dark) currents. This enhances the sensitivity by many orders of magnitude, but it is important to set the

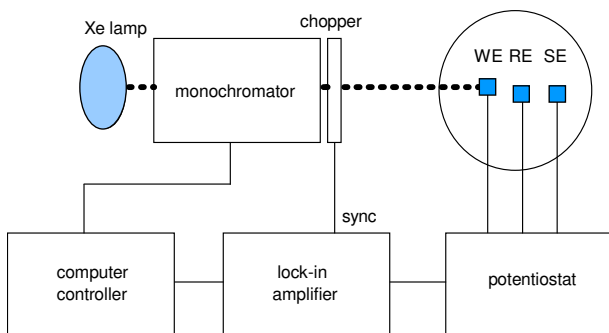


Figure 12.6 Experimental arrangement for photocurrent spectroscopy.

phase of the lock-in amplifier using a photodiode in place of the sample since the photocurrent response of the sample to chopped illumination may show transient effects due, for example, to surface recombination. In such cases, the in-phase and 90° components (or alternatively the amplitude and phase) of the photocurrent can be recorded. The origin and interpretation of phase shifts in the photocurrent response are discussed in Section 12.7.1, which deals with intensity-modulated photocurrent spectroscopy (IMPS). Problems with the use of chopped illumination also arise when the photocurrent response is slow. An example of this kind of behaviour is provided by dye-sensitised nanocrystalline solar cells, discussed in Chapter 8, where the photocurrent rise-time depends on illumination intensity (O'Regan and Grätzel, 1991; Peter and Vanmaekelbergh, 1999). The rise-time of these cells can be as slow as several seconds if low light intensities are used in conventional photocurrent spectroscopy (Peter and Wijayantha, 1999). There are two ways to solve this problem. The first is to use 'DC' (*i.e.* unchopped) illumination. The second is to superimpose the chopped monochromatic radiation on a much higher steady illumination level that guarantees that the photocurrent response is fast enough to avoid errors. In general., however, the lowest possible chopping frequency (typically a few Hz) should be used.

The use of chopped illumination and lock-in detection can cause problems of interpretation. It is advisable to measure the dark current in order to establish that it is negligible compared with the photocurrent. There are many reports of 'photo-responses' in the literature that are of questionable validity. Thermal effects may be significant if high-intensity light is used. The 'photocurrent' in this case arises from modulation of the dark current by the light-induced temperature change. Thermal effects can often be recognised by the fact that the response becomes smaller as the chopping rate is increased: a dependence on the inverse square root of the chopping frequency is predicted theoretically. Not all photocurrent responses are due to photoelectrochemical reactions at the interface. In many systems, such as polymer-modified electrodes, the main effect of generation of electrons and holes may be to increase the bulk conductivity (photoconductivity). Photoconductivity effects can be distinguished from photovoltaic effects by the fact that the photocurrent is not a linear function of the incident photon flux; often it depends on the square root of intensity as a consequence of electron/hole recombination in the bulk. Photoconductivity excitation spectra tend to exhibit a maximum at the absorption edge of the material, where the penetration depth of the light is comparable with the sample thickness. The photocurrent is smaller at shorter wavelengths because the light is absorbed close to the surface. Unfortunately, insufficient attention has been paid to these distinguishing criteria in many photoelectrochemical studies.

Before photocurrent excitation spectra can be normalised to allow for the wavelength dependence of the illumination intensity, it is essential to establish the relation between the photocurrent response and the incident photon flux. This can be done using calibrated neutral density filters. The relationship is generally not linear for photoconductive systems or for systems in which processes such as surface recombination or photocurrent multiplication occur (Peter, 1990). The incident photon flux can be measured using a UV-enhanced silicon photodiode with known sensitivity.

The sensitivity of photocurrent spectroscopy can be enhanced in a number of ways. A Faraday cage can be used to eliminate electrical interference, and it is useful to use a battery-operated potentiostat constructed using low-noise operational amplifiers. The voltage-generated current noise in the system depends on the electrode capacitance, so measurements on metal electrodes are particularly prone to noise problems. Since high-resistance reference electrodes can introduce noise, it is advisable to carry out measurements in two-electrode mode using a large non-polarisable counter electrode such as a palladium/hydrogen electrode. Photoemission currents as low as 10^{-10} A have been measured in this way (Rudge *et al.*, 1994).

Photocurrent spectroscopy is a useful tool for the determination of bandgapsof in semiconductor alloys (Hutton and Peter, 1993) or surface films on metals (Peter, 1980, 1987 and 1989; Campbell *et al.*, 1992). Figure 12.7 illustrates the composition dependence of the photocurrent onset energy for a series of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloy samples (Hutton and Peter, 1992). The relationship between bandgap and composition is known for this system, so photocurrent spectroscopy is a convenient tool for compos-

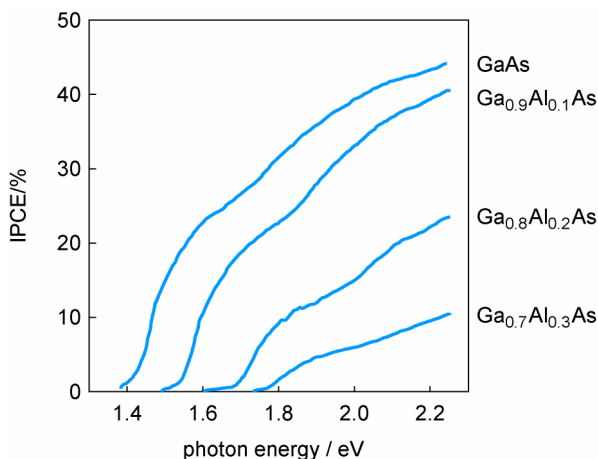


Figure 12.7 Photocurrent spectra for a series of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloy samples, showing the shift in bandgap energy. Adapted from Hutton and Peter (1992).

itional analysis. The bandgap is found by using the relationship between the absorption coefficient α and photon energy $h\nu$ for a direct-gap semiconductor

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (12.5)$$

Expansion of the Gärtner equation (eq. 12.2) for small values of α shows that the photocurrent is a linear function of the absorption coefficient near the band edge. The bandgap can therefore be obtained using the plot illustrated in Fig. 12.8.

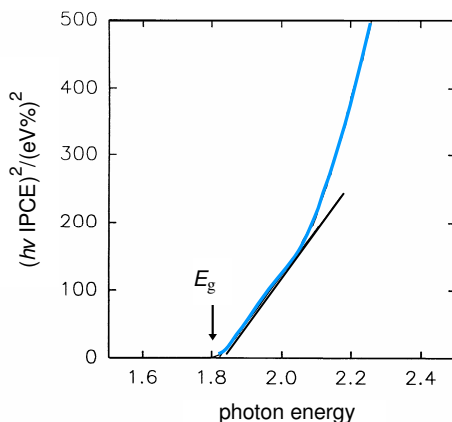


Figure 12.8 Direct-bandgap plot for $\text{Ga}_{0.7}\text{Al}_{0.3}\text{As}$ used to determine the bandgap. Adapted from Hutton and Peter (1993).

Figure 12.9 illustrates the application of photocurrent spectroscopy to the study of anodic films on metals. In this case the system is anodised bismuth, covered by a thin (few nm) layer of amorphous insulating oxide. The photocurrent spectra reveal that photoemission from the metal into the oxide occurs as well as electron/hole generation by band-to-band photoexcitation (Castillo and Peter, 1983). Photocurrents of both signs can be observed because bismuth oxide is an insulator. The spectrum of the anodic photocurrent corresponds to band-band excitation, and shows that the bandgap of the oxide is 2.8 eV. The spectrum for the cathodic photocurrent also shows the band-band component above 2.8 eV, but an additional response is seen to extend down to much lower energies corresponding to half the bandgap. This part of the photocurrent spectrum arises from internal photoemission of electrons from the bismuth into the oxide. The onset energy of 1.4 eV indicates that the Fermi level in the oxide is located in middle of the bandgap, as expected for an insulator. Figure 12.10 illustrates the treatments of the photocurrent data used to extract the values of the bandgap (2.8 eV) and the photoemission barrier height (1.4 eV).

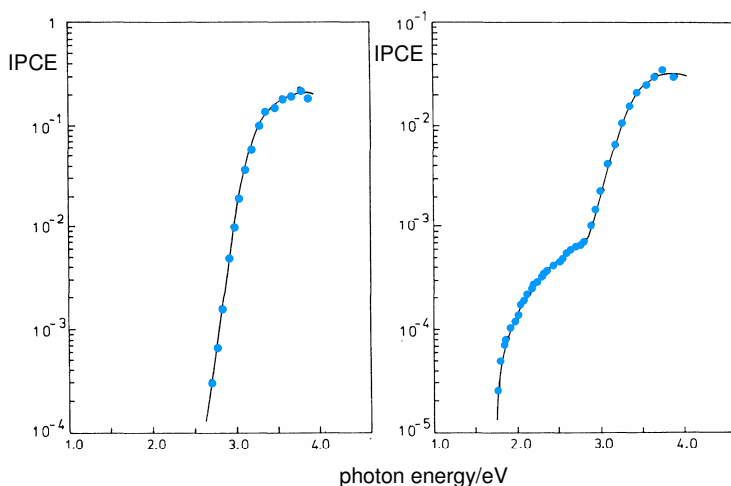


Figure 12.9 Photocurrent spectra for anodic oxide films on bismuth. The left-hand spectrum is for the anodic photocurrent and the right-hand spectrum is for the cathodic photocurrent. Note the additional low-energy response due to internal photoemission at the Bi/Bi₂O₃ interface. Adapted from Castillo and Peter (1983).

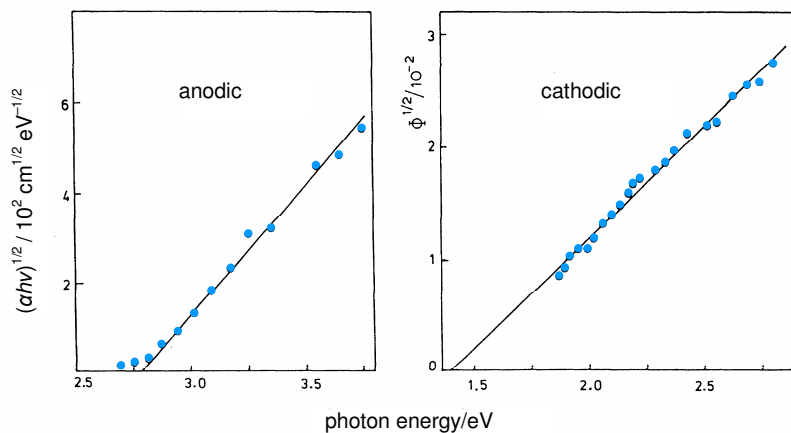


Figure 12.10 Plots of the anodic and cathodic photocurrent spectra for anodised bismuth, showing how the bandgap and photoemission threshold are obtained. Adapted from Castillo and Peter (1983).

Photocurrent spectroscopy can be used to determine the minority-carrier diffusion length of semiconductors. The Gärtner equation (eq. 12.2) can be written in the linear form

$$-\ln\left(1 - \frac{i_{\text{photo}}}{qj_0}\right) = \ln(1 + \alpha L) + \alpha W \quad (12.6)$$

Since the width W of the space-charge region is proportional to $(E - E_{\text{fb}})^{1/2}$ (cf. eq. 12.3), it follows that a plot of $\ln(1 - i_{\text{photo}}/qj_0)$ vs. $(E - E_{\text{fb}})^{1/2}$ can be used to derive α and L . The method works best for indirect-gap semiconductors such as GaP (Li *et al.*, 1984; Peat and Peter, 1987) where the penetration depth $1/\alpha$ of the light exceeds W by at least an order of magnitude. The method is less accurate for direct-gap materials. The main problem is that the condition $W > 1/\alpha$ is fulfilled only for small values of band bending near the flatband potential. The photocurrent in this region is often reduced by surface recombination, so that plots based on eq. 12.6 are unreliable. In some cases, surface recombination can be suppressed by choosing a fast scavenger to prevent photodecomposition reactions. A good example of a fast hole scavenger is Na_2SO_3 , which has been used to stabilise $n\text{-CdS}$ so that the photocurrent–potential plot follows the Gärtner equation down as far as the flatband potential (Fermin, 1997). Alternatively, intensity-modulated photocurrent spectroscopy can be used to eliminate the effects of surface recombination (Peat and Peter, 1987).

12.3.2 Photovoltage spectroscopy

Photovoltage spectroscopy is used less frequently than photocurrent spectroscopy, but it has played an important role in commercial semiconductor characterisation systems. It has been used, for example, to determine the bandgap of ternary or quaternary III–V semiconductors. The main drawback of the method is that the relationship between the photovoltage and the absorbed photon flux is non-linear. However, it can be shown that near the band edge (small absorption coefficient), the photovoltage is a linear function of the absorption coefficient α . Figures 12.11 and 12.12 illustrate the use of photovoltage spectroscopy to determine the bandgap (and hence the composition) of epitaxial layers of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloy samples (Hutton and Peter, 1993).

Photovoltage spectra are measured at open circuit using chopped light of low intensity. It might appear that an advantage of photovoltage spectroscopy over photocurrent spectroscopy is that no photocorrosion occurs. However, this is not necessarily correct, because anodic photocorrosion in the illuminated areas may be balanced by cathodic reduction of solution species such as oxygen or protons.

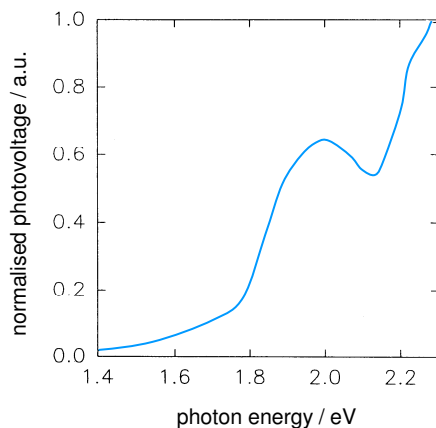


Figure 12.11 Photovoltage spectrum of $\text{Ga}_{0.7}\text{Al}_{0.3}\text{As}$ in $0.1 \text{ mol dm}^{-3} \text{ KOH}$. Adapted from Hutton and Peter (1993).

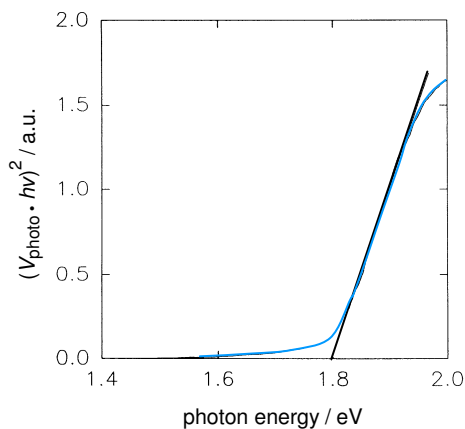


Figure 12.12 Plot used to obtain the bandgap of $\text{Ga}_{0.7}\text{Al}_{0.3}\text{As}$ from the photovoltage spectrum in Fig. 12.11. Adapted from Hutton and Peter (1993).

Hutton and Peter (1993) in a study of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ compared the bandgap values derived from photocurrent and photovoltage spectra with those derived by electrolyte electroreflectance spectroscopy (EER). They concluded that EER gives the most reliable results, provided that the doping density is not too high.

12.3.3 Light-induced microwave reflectance changes

Currents measured in photoelectrochemical or photovoltaic experiments as a function of potential reflect the action of electrical fields on electrical charges and dipoles. The information obtained from conventional measurements is limited since it is not possible to distinguish experimentally between displacement currents and currents associated with charge transfer. Microwaves interact via their periodical electrical fields with electrical charges and dipoles. Microwave conductivity measurements of semiconductor electrodes sense changes in the density of free electronic charge carriers arising from illumination (or from changes in potential: Section 12.3.4). They can therefore be used to provide complementary information (for a review of microwave photoelectrochemistry, see Bogomolni *et al.*, 1982; Schlichthörl and Tributsch, 1992; Tributsch *et al.*, 1993; Tributsch, 1999). The combination of photoelectrochemical and microwave conductivity measurements allows much better definition of the system, so reaction constants and mechanisms can be determined quantitatively.

Figure 12.13 illustrates a versatile experimental set-up for microwave conductivity measurements with the microwave source (8–40 GHz), a circulator and a detector, which monitors the microwave energy reflected from the electrochemical or photovoltaic cell. The cell and electrode geometries are designed in such a way that the microwave power can reach the energy-converting interface (losses in metal contacts or aqueous electrolyte should be minimised). Depending on the experimental conditions, time-resolved, space-resolved or potential-dependent measurements are possible as well as combinations (for further details, see Schlichthörl and Tributsch, 1992; Wünsch *et al.*, 1996; Chaparro and Tributsch, 1997; Tributsch, 1999).

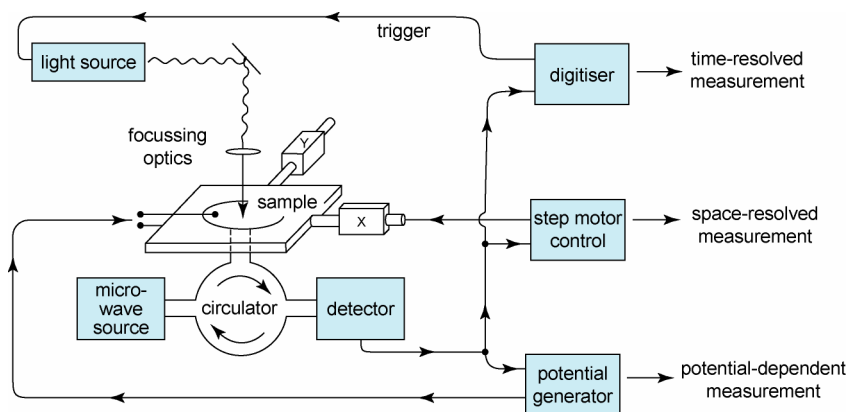


Figure 12.13 Experimental arrangement for microwave electrochemistry for time-resolved, space-resolved and potential-dependent measurements (and combinations).

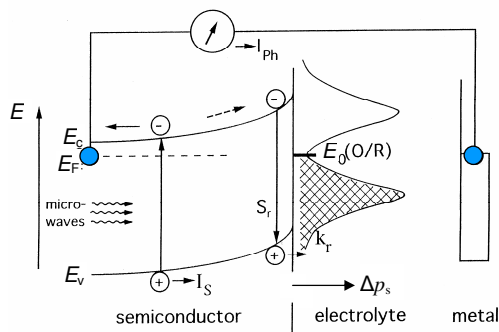


Figure 12.14 Band diagram of the semiconductor–electrolyte interface, illustrating photogeneration and loss of minority carriers (holes) via surface recombination and interfacial electron transfer. The balance between these processes determines the steady-state surface concentration of minority carriers Δp_s .

Figure 12.14 shows the energy scheme of a semiconductor in contact with an electrolyte. The excitation process as well as interfacial charge transfer and surface recombination reactions are indicated. Holes generated by illumination accumulate at the interface, and their concentration is determined by the balance between generation on the one hand and recombination and interfacial charge transfer on the other. In effect, holes ‘queue’ at the surface because the rates of recombination and charge transfer are finite. The surface concentration of photogenerated minority carriers, Δp_s , plays a significant role in the analysis. The measured photocurrent i_{photo} is related formally to Δp_s by the expression

$$i_{\text{photo}} = qk_{\text{ct}}\Delta p_s \quad (12.7)$$

where k_{ct} (cm s^{-1}) is the rate constant for the interfacial charge-transfer reaction.

If recombination in the neutral region is negligible, the steady-state concentration of minority carriers in the surface region (cm^{-3}) is determined by the incident photon flux j_0 ($\text{cm}^{-2} \text{s}^{-1}$) and the rate constants for interfacial charge transfer k_{ct} and surface recombination k_{rec} (both cm s^{-1}).

$$\Delta p_s = \frac{j_0}{k_{\text{ct}} + k_{\text{rec}}} \quad (12.8)$$

In practice, the incident illumination is chopped or intensity-modulated to enhance the detection of the photoinduced microwave conductivity (PMC) signal, so that the measurements are not strictly steady state. However, the chopping frequency is normally much lower than the characteristic frequency associated with the relaxation

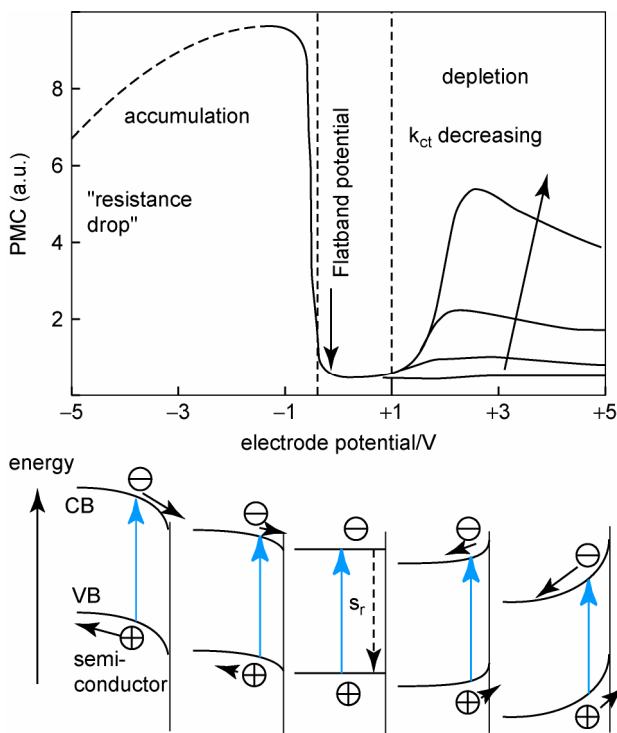


Figure 12.15 Predicted PMC behaviour as a function of band bending (*n*-type sample). Note that the response is largest under accumulation conditions since minority carriers diffuse away from the interface.

of the surface concentration Δp_s by charge transfer and recombination, so that the approximation is valid.

The microwave conductivity is proportional to the number of free electronic charge carriers multiplied by their respective mobilities (the contribution of ions and dipoles can be neglected in a first approximation.). The microwave sensitivity constant S must be obtained by calibration. The potential-dependent photoinduced microwave conductivity (PMC) of a semiconductor resulting from illumination has been calculated analytically as a function of the interfacial charge-transfer and surface recombination rates (Schlichthörl and Tributsch, 1992). The starting point is the general set of equations of the form

$$\text{PMC} = S \sum_i \Delta n_i u_i q = f(k_{\text{ct}}, k_{\text{rec}}) \quad (12.9)$$

where u_i is the mobility of charge carriers i and Δn_i is the number density of photogenerated charge carriers. Since the potential dependences of the photocurrent and of the light-induced microwave conductivity of a semiconductor junction can be measured simultaneously, the microwave equations contain three unknown variables: the surface concentration Δp_s of minority carriers, the rate constant for surface recombination k_{rec} and the interfacial charge-transfer rate constant k_{ct} . These can therefore be evaluated quantitatively, provided the microwave sensitivity factor S is measured experimentally or is calculated in the case of simple geometries.

The following simple relation between photocurrent and the interfacial charge-transfer rate can be obtained for larger band bending (ΔE is the energy band bending):

$$\text{PMC} = S \cdot f(\Delta E) \approx \Delta p_s \Phi(\Delta E) \approx \frac{i_{\text{photo}}}{k_{\text{ct}} (\Delta E)^{1/2}} \quad (12.10)$$

The interfacial charge-transfer rate k_{ct} can therefore be determined to a first approximation via the relation

$$k_{\text{ct}} = \frac{i_{\text{photo}}}{\text{PMC}(\Delta E)^{1/2}} \quad (12.11)$$

which shows that k_{ct} depends only on the photocurrent, the microwave conductivity, and the electrode potential.

The analysis indicates that the results of light-induced microwave conductivity measurements should look very different from the familiar photocurrent–voltage plots. This is clear from Fig. 12.15, which relates the PMC signal to the band bending. In general, the PMC response exhibits the following features: in the region on the right-hand side where the photocurrent starts to rise towards the photocurrent saturation region, a pronounced peak occurs in the microwave conductivity. The size of the peak depends on the rate of interfacial charge transfer: it is large when the charge-transfer rate is small (build-up of minority carriers at the interface). It disappears when charge transfer is so fast that the build-up of minority carriers is negligible. These trends have been clearly demonstrated with silicon interfaces covered with oxide layers of variable thickness. A minimum in the microwave conductivity signal is found near the flatband potential as the result of the consumption of minority carriers by surface recombination. By contrast, the light-induced microwave conductivity increases again in the accumulation region because photogenerated minority carriers diffuse into the interior of the semiconductor where they recombine at a rate determined by their bulk lifetime. It is particularly interesting to note that photoinduced microwave conductivity signals can easily be detected under accumulation conditions, whereas the photocurrent is zero.

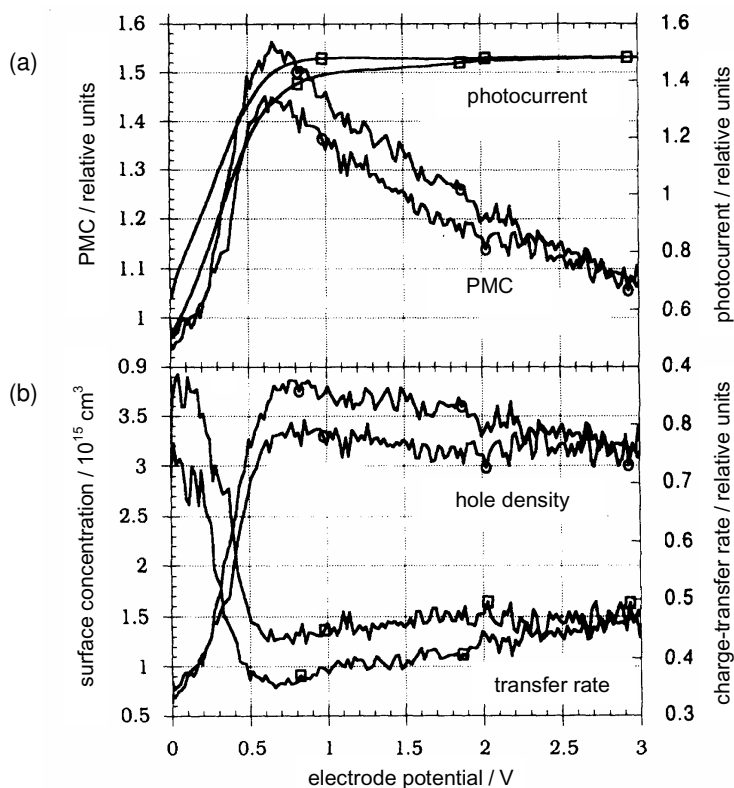


Figure 12.16 (a) Photocurrent and PMC plots for *n*-Si in 0.2 M NH_4F ; (b) calculated hole density at the surface and electron-transfer rate. Adapted from Schlichthörl and Tributsch (1992).

Schlichthörl and Tributsch (1992) have given examples of experimental PMC responses for *n*-Si in NH_4F solutions. Figure 12.16 shows the relationship between the photocurrent and the PMC response, as well as the calculated density of holes 'queuing' at the surface and the relative changes in the hole-transfer rate. For *n*-Si in contact with 0.6 M NH_4F , the interfacial charge-transfer rate is sufficiently high to prevent holes queuing, and the PMC response in the depletion region falls to zero. When the NH_4F concentration is reduced to 0.2 M, a measurable PMC response appears near the onset of the anodic photocurrent, indicating that hole transfer is slower, possibly as the result of the formation of a thin oxide layer. Sustained photocurrent oscillations at silicon electrodes can be triggered at sufficiently high potentials, and in this case the photocurrent and PMC response oscillate synchronously (Lewerenz and Schlichthörl, 1994).

The influence of deposited Pt nanoparticles on the interfacial kinetics of silicon has been investigated by combining photocurrent and PMC measurements (Wünsch *et al.*, 1996). Solid electrolyte contacts to silicon have also been studied, and it has been found that the PMC signal follows the same potential dependence as with liquid electrolytes. It has been shown that by electropassivating the silicon/electrolyte interface the bulk minority-carrier lifetime of silicon wafers can be determined from the PMC plateau in the accumulation region (Schulenberg and Tributsch, 2000).

12.3.4 Potential-modulation-induced microwave reflectance

Since the density of free charge carriers at the semiconductor/electrolyte contact depends on potential, modulation of the potential gives rise to a corresponding modulated microwave reflectance response. The potential-modulated microwave reflectance method has been developed to deconvolute the impedance of semiconductor electrolyte interfaces. Its main advantage is that it is sensitive only to free carriers, whereas conventional impedance measurements cannot distinguish readily between free and trapped carriers. The method has been used to investigate the behaviour of the silicon/electrolyte interface under both depletion (Schlichthörl and Peter, 1994 and 1995) and inversion (Schlichthörl and Peter, 1995) conditions.

It can be shown that the small-amplitude potential-modulated microwave response ΔR_M under depletion conditions is related linearly to the space-charge capacitance C_{sc} by

$$\Delta R_M = S u C_{sc} \Delta U / d \quad (12.12)$$

where S is the sensitivity factor, u the majority-carrier mobility, ΔU the potential modulation and d the sample thickness. It follows that plots of $1/\Delta R_M^2$ should be equivalent to Mott–Schottky plots (*cf.* Section 12.2.1)

Figure 12.17 compares the capacitance response of the silicon/fluoride solution interface at pH 1.3 with the potential-modulated microwave response. The shoulder in the capacitance curve due to surface states is absent from the microwave reflectance curve. The Mott–Schottky plot for ΔR_M extends to the flatband potential, whereas the plot of $1/C^2$ deviates in the region where the surface-state capacitance becomes important. Comparison of the capacitance and microwave responses allows deconvolution of the surface-state capacitance (Schlichthörl and Peter, 1994 and 1995).

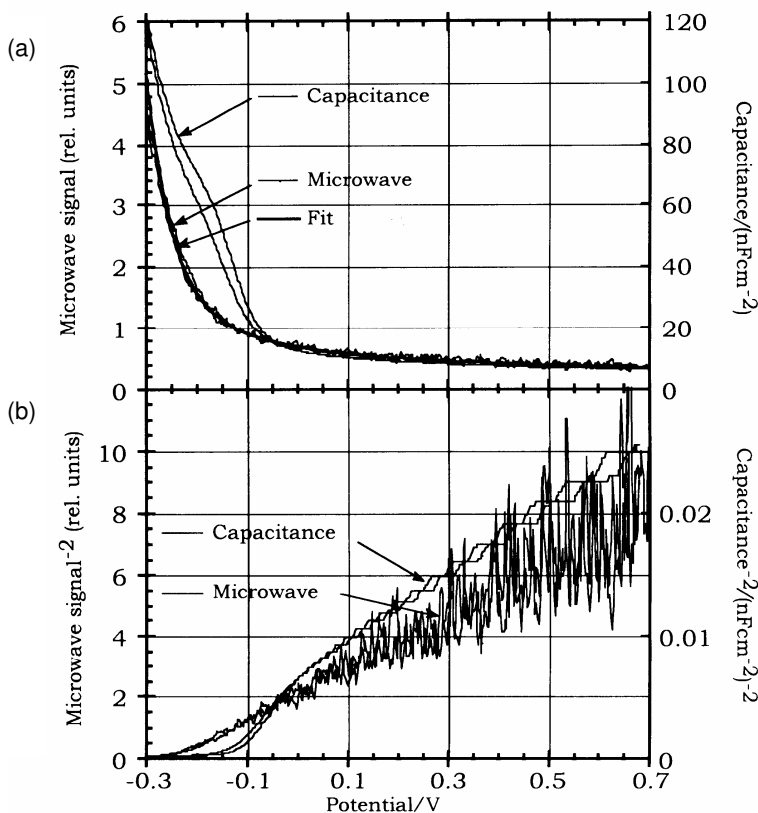


Figure 12.17 (a) Variation of capacitance and ΔR_M with potential for *n*-Si(111) in NH_4F (pH 1.3). (b) Mott-Schottky plots of capacitance and ΔR_M data.

12.4 In-situ spectroscopic methods

12.4.1 In-situ UV/visible methods

A wide range of spectroelectrochemical techniques has been developed to study solution-phase and surface electrochemistry. UV/visible spectroscopy can be performed either in transmission mode if the substrate electrode is transparent or in reflectance mode if the substrate is opaque and sufficiently reflective. Changes in the composition of the surface or solution that are a consequence of electrode reactions can be followed by monitoring the absorption or reflectance. Diode array spectro-

meters or spectrographs with CCD array detectors allow spectra to be rapidly accumulated, so that the evolution of spectra in time can be monitored as the reaction proceeds. Alternatively, the reflectance or absorbance can be measured at a chosen wavelength as a function of time or applied potential. The sensitivity can be enhanced by using potential-modulation techniques. Sampling techniques are used to obtain spectra for the analysis of laser-induced photochemical processes on very short (femtosecond and picosecond) time scales.

An interesting example of the application of UV/visible methods in photoelectrochemistry is provided by the detection of electron accumulation in nanocrystalline TiO_2 electrodes (Rothenberger *et al.*, 1992; Boschloo and Fitzmaurice, 1999). These electrodes are used in dye-sensitised nanocrystalline solar cells, and it is important to know the energy of the conduction band when discussing the sensitisation process. Mott-Schottky plots cannot be used for this purpose since the particle size is smaller than the Debye length (Peter and Vanmaekelbergh, 1999). When the electrode potential is made sufficiently negative, the Fermi energy of the substrate electrode is raised to the level of the conduction band of TiO_2 and electrons are injected into the nanocrystalline phase from the substrate. These electrons, which may be trapped or free, can be detected by their optical absorbance, which extends from the visible into the near infrared. This is an example of electrochromism. Electrons injected by photoexcitation of an adsorbed dye can also be detected in the same way since the electron absorption can be monitored at wavelengths beyond the absorption edge of the dye (Franco *et al.*, 1999).

12.4.2 *In-situ infrared methods*

The introduction of *in-situ* infrared spectroscopy to electrochemistry has revolutionised the study of metal/electrolyte interfaces. Modulation or sampling techniques are applied in order to enhance sensitivity and to separate surface species from volume species. Methods such as EMIRS (electrochemically modulated IR spectroscopy) and SNIFTIRS (subtractively normalised interfacial Fourier Transform infrared spectroscopy) have been employed to study electrocatalytic electrodes, for example. There have been surprisingly few studies of the semiconductor/electrolyte interface by infrared spectroscopy. This because up to now little emphasis has been placed on the molecular electrochemistry of electrode reactions at semiconductors because the description of charge transfer at semiconductor/electrolyte interfaces is derived from solid-state physics. However, the evident need to identify the chemical identity of surface species should lead to an increase in the application of *in-situ* FTIR.

Metal electrodes can be studied by IR spectroscopy using specular reflectance in a cell in which the metal electrode is pressed against an infrared transparent window, trapping a thin layer of electrolyte. Polarised infrared light passes through the window and is reflected back from the electrode. An alternative approach aimed at increasing surface sensitivity takes advantage of multiple reflection in attenuated total internal reflection (ATR) prisms fabricated from an infrared transparent material such as silicon or zinc selenide. The electrochemical interface to be investigated is deposited onto one surface of the prism, and the evanescent wave arising from internal reflection samples the investigated interface and provides a measurable infrared absorbance signal. The main problem with the ATR method is the difficulty in preparing suitable electrochemical interfaces on the prism. Either the total reflecting crystal (*e.g.* silicon) is contacted, or a metallic grid or a thin-layer metal contact is put between the total reflecting crystal and the electrode layer. In the first case, a relatively high internal ohmic resistance has to be taken into consideration because the ATR crystal must be undoped in order to allow passage of infrared light. In the second case, the grid between the total reflecting crystal and the electron layer has to be tailored in such a way as to allow penetration of the evanescent wave to the material/electrolyte interface. Alternatively the metal layer has to be very thin and highly conducting (gold). The ATR technique has been applied successfully in situations where product analysis is important. A recent example is an *in-situ* study of the stability of photosensitiser molecules in functioning dye sensitisation cells (Grunwald and Tributsch, 1997). Figure 12.18 shows the experimental setup. At a wavelength of $5\text{ }\mu\text{m}$, the penetration depth of the evanescent wave into the nanocrystalline TiO_2 matrix is of the order of $1.5\text{ }\mu\text{m}$, so that a significant fraction of the active sensitised layer adjacent to the metallic contact can be sampled.

FTIR has been used to study the silicon/electrolyte interface. The formation of porous silicon on *n*-Si during photoetching in fluoride media can readily be followed since the hydrogen-terminated surface is identified by the Si-H stretch bands centred around 2100 cm^{-1} (Peter *et al.*, 1989; Peter *et al.*, 1990a). Similarly, the transition from a hydrogen-terminated to an oxide-covered surface during electropolishing has been followed by *in-situ* infrared spectroscopy (da Fonseca *et al.*, 1996 and 1997).

In principle, IR methods can be used to monitor photogenerated carriers in the same way as microwave reflectance methods. However, PMC can detect changes in carrier density as low as 10^9 cm^{-3} , whereas the sensitivity of IR is typically six orders of magnitude worse.

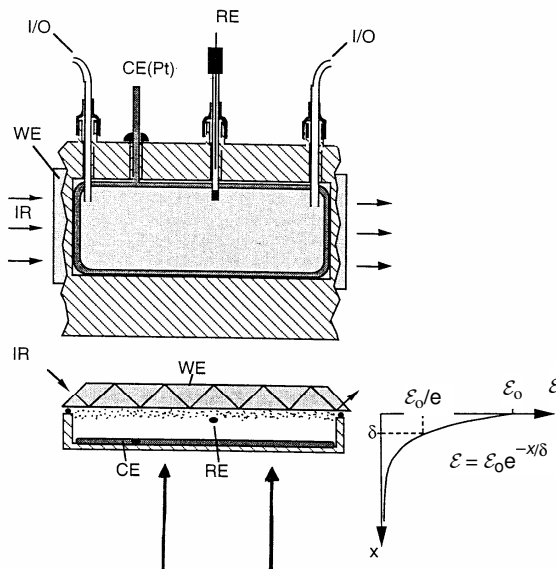


Figure 12.18 Electrochemical cell and silicon ATR element coated with dye-sensitised TiO_2 . The electric field distribution $\mathcal{E}$ in the evanescent wave is also shown.

12.4.3 Luminescence spectroscopy

In-situ luminescence measurements have been used to study the semiconductor/electrolyte interface for many years (*e.g.* Petermann *et al.*, 1972). Luminescence may result from optical excitation of electron/hole pairs that subsequently combine with the emission of light (photoluminescence). Alternatively, minority carriers injected from redox species in the electrolyte can recombine with majority carriers and give rise to electroluminescence. The review by Kelly *et al.* (1999) summarises the main features of photoluminescence (PL) and electroluminescence (EL) at semiconductor electrodes. The experimental arrangements for luminescence measurements are relatively straightforward. Suitable detectors include a silicon photodiode placed close to the sample, a conventional photomultiplier or a cooled charge-coupled silicon detector (CCD). The CCD system is used with a grating spectrograph to obtain luminescence spectra.

PL measurements have been used to obtain information about the distribution of charge and potential at semiconductor/electrolyte junctions. In the ideal case, the Gärtner equation (eq. 12.2) can be used to derive the potential dependence of the PL

intensity. The separation of electron/hole pairs in the space-charge region is very rapid: only those pairs created deeper in the semiconductor can recombine radiatively. Since electron/hole pairs created within a diffusion length of the edge of the space-charge region are also collected by diffusion, a so-called ‘dead layer’ of thickness $(W + L)$ is formed. The PL intensity I_{PL} is given by

$$I_{\text{PL}} = \frac{\kappa j_0 e^{-\alpha W}}{1 + \alpha L} \quad (12.13)$$

where κ is the efficiency of radiative recombination, and the other terms are the same as those in the Gärtner equation. For more realistic calculations, kinetic parameters taking account of interfacial charge transfer rate and surface recombination rate, have to be considered and the Gärtner equation as well as eq. 12.13 have to be extended. A simple way to do this is outlined in (Tributsch, 2001).

Luminescence may also arise as a consequence of electrode reactions at semiconductors that result in injection of minority carriers under accumulation conditions (see references in Kelly *et al.*, 1999). An interesting example is the efficient red electroluminescence observed during the reduction of persulphate ions at a porous silicon layer on *n*-Si (Meulenkamp *et al.*, 1995). Here the luminescence arises from electron/hole recombination, and the holes are injected by the persulphate radical ion according to the scheme



The luminescence appears in the visible because the dimensions of the ‘quantum wires’ making up the porous silicon skeleton are so small that quantum confinement effects increase the bandgap from the bulk value of 1.1 eV. The luminescence spectra shown in Fig. 12.19 were obtained using a cooled silicon CCD array spectrograph that allows rapid sampling (20 spectra s^{-1}). The observed potential-dependent tuning of the PL and EL emission spectra is attributed to the size dependence of electron occupation that arises from the quantum confinement in very small particles (Meulenkamp *et al.*, 1995). Since smaller particles have higher bandgaps, their conduction band levels are higher than those of larger particles. As a consequence, electrons are more likely to populate the larger particles, quenching the electron/hole pair by the Auger process. Since the larger particles emit at longer wavelengths, the emission is progressively quenched from the long wavelength end as the potential is

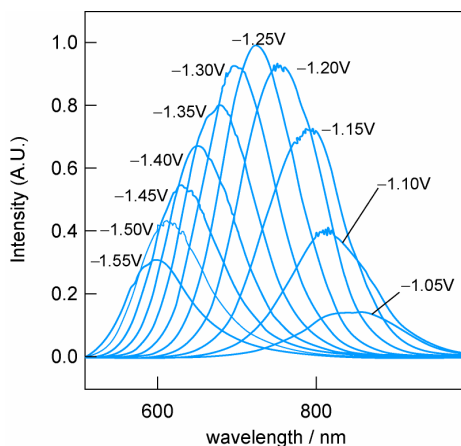


Figure 12.19 Voltage-tuned electroluminescence from porous silicon recorded using a CCD spectrograph. Electrolyte $0.2 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_8 + 1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. Adapted from Meulenkamp *et al.* (1995).

made more negative. This process has been modelled to predict PL and EL spectra (Meulenkamp *et al.*, 1995).

Potential-dependent photoluminescence experiments provide information not only on quantum efficiencies but also on radiative or non-radiative recombination centres. Luminescence images of electrodes can be produced with the same set-ups that are used for photocurrent or microwave conductivity imaging, with the additional installation of a photodetector or photomultiplier for the measurement of luminescence. As with other imaging experiments, the observed images may show a luminescence distribution that depends strongly on applied electrode potential (see Section 12.8).

12.5 Time-resolved optical and spectroscopic techniques

12.5.1 Time-resolved photocurrent and photovoltage measurements

Generation, transport and reaction of charge carriers in semiconductor/electrolyte systems can be studied using pulsed laser excitation. Details can be found in reviews by Peter (1990) and Peter and Vanmaekelbergh (1999) and in papers by Willig and co-workers (Bitterling and Willig, 1986). For measurements at very short times, it is necessary to design the electrochemical cell to minimise stray capacitance and inductance.

The photocurrent response of conventional semiconductor electrodes to pulsed laser excitation is predominantly determined by the RC time constant of the cell. The capacitance C_{scI} is typically of the order of 10^{-8} – 10^{-7} F, and the resistance is determined by the sum of the cell and measuring resistances (typically 10–100 Ω). At short times ($t < RC$), the measured response corresponds to the photovoltage generated by the laser pulse. In order to observe charge separation, it is necessary to make measurements at times shorter than 100 ps (Willig *et al.*, 1987). The subsequent decay is determined by the RC time constant. For small-amplitude perturbations, the current decay is exponential. For larger perturbations (higher incident laser power), the response is no longer exponential since C_{scI} is potential-dependent and also because second-order electron-hole recombination can occur. The transients are also influenced by surface electron recombination, which effectively discharges C_{scI} by inducing a flux of majority carriers to the surface (Peter, 1990). The rate of transfer of minority carriers across the semiconductor/electrolyte interface is not accessible to measurement by transient photocurrent techniques. By contrast, time- or frequency-resolved microwave measurements can be used for this purpose because they monitor changes in the density of free charge carriers as they transfer to the solution or recombine.

The transient photocurrent response of porous nanocrystalline oxide electrodes is quite different from that of bulk semiconductor electrodes. The main reason for the difference is that the interconnected nanoparticles are in contact with a permeating electrolyte that shields electrostatic interaction effectively. As a consequence, electron transport occurs by diffusion rather than by drift. Electron diffusion is strongly influenced by trapping states, so that the electron diffusion coefficient D_e in the nanocrystalline material is orders of magnitude smaller than in the bulk solid. D_e is also dependent on the light intensity, so that large-amplitude photocurrent responses are difficult to model. The simplest approach is to superimpose a low-intensity laser pulse on steady background illumination (Duffy *et al.*, 2000c). In this situation, D_e can be treated as a constant. Figure 12.20 shows examples of small-amplitude current transients for a dye-sensitised TiO_2 cell. In the absence of DC illumination, the photocurrent response is very slow and dominated by thermal release of trapped electrons from deep trapping states. However, when DC bias illumination is used, electron transport occurs via shallow traps and a much faster pulse response is observed. Peter and Vanmaekelbergh (1999) give further details of electron transport in nanocrystalline photoelectrodes. It is important to realise that the apparent electron diffusion coefficients determined from the transient or periodic photocurrent responses of nanocrystalline solar cells do not correspond to the diffusion coefficient of free electrons in the conduction band of the oxide. In general, the apparent electron

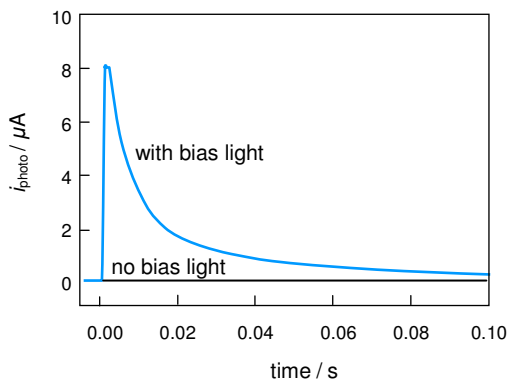


Figure 12.20 Small-amplitude photocurrent transients for a dye-sensitised TiO_2 cell, showing the effect of DC bias illumination.

diffusion coefficients are orders of magnitude smaller as a consequence of the slow adjustment of the population of electrons in traps. The same effect influences the apparent lifetime of electrons in dye-sensitised cells: in this case the lifetime appears to be much longer than the true lifetime of electrons in the conduction band of the oxide. Electron transport and electron transfer in dye-sensitised nanocrystalline solar cells have been reviewed recently by Peter (2007).

12.5.2 Time-resolved spectroscopic measurements

The techniques for transient absorbance spectroscopy are well established, and they will not be described here. They are widely used to detect transient intermediates formed in photoelectrochemical reactions. A particularly interesting application of transient absorbance measurements is to follow the processes taking place in dye-sensitised nanocrystalline solar cells. These cells operate by injection of electrons into nanocrystalline TiO_2 by a photoexcited sensitizer dye. Regeneration of the dye from its oxidised state is usually achieved using the iodide/tri-iodide redox couple. The kinetics and mechanism of the reactions have been studied by detecting the transient absorbance due to the oxidised dye and intermediates such as I_2^- in the regeneration reaction (Nasr *et al.*, 1996; Durrant *et al.*, 1997 and 1999). Time-resolved luminescence (PL and EL) measurements are less common, although in principle they can be informative (Kelly *et al.*, 1999). Time-resolved infrared spectroscopy is another interesting technique that is now possible because of developments in FTIR systems.

12.5.3 Time-resolved microwave reflectivity measurements

The microwave reflectivity of a semiconductor depends on the sample conductivity, *i.e.* on the density and mobility of free electrons and holes. Photoexcitation of the sample brings about an instantaneous increase of electron and hole densities and a corresponding change in microwave reflectivity. After excitation by a laser pulse, the decay of minority carriers by bulk and surface recombination, as well as by trapping, can be followed by the change in microwave reflectivity. For small changes in carrier density, the relationship between microwave reflectivity and carrier density is linear.

The time-resolved microwave reflectivity (TRMR) technique is well established for contactless characterisation of minority-carrier lifetimes in semiconductors. It can be applied to map surface recombination; in this case the sample is moved by an X–Y stage to allow spatially resolved measurement of the minority-carrier lifetime.

Time-resolved photoinduced microwave conductivity measurements can be made as a function of applied potential. It has been shown that the measured minority-carrier lifetime τ for moderately fast or slow interfacial charge transfer depends not only on the interfacial rate constant and surface recombination k_{rec} , but also on the energy band bending (ΔE) and the Debye length L_D (Tributsch, 1999).

$$\tau = \frac{0.114L_D}{(k_s + k_{\text{rec}})(\Delta E)^{1/2}} \quad (12.17)$$

Experimentally, the lifetime depends markedly on the potential, showing a minimum near the flatband potential and increasing towards positive and negative potentials. This is consistent with the behaviour of the steady state PMC signals (see Section 12.3.3), but corrected by a potential-dependent term (Tributsch, 1999). For *n*-type electrodes, a maximum in the lifetime is observed at potentials positive from the flatband potential, as found with silicon in contact with propylene carbonate or ion-conducting polymers (Schulenburg *et al.*, 2000). An important feature of time-resolved PMC measurements is that they are not limited by the *RC* time constant, which usually determines the time resolution in photoelectrochemical measurements (see Section 12.5.1 and Peter and Vanmaekelbergh, 1999). Faster processes that are not controlled by charge or discharge of the interfacial capacitance can therefore be seen. The theoretical limit for time-resolved measurements for microwave frequencies up to 40 GHz is 25 ps. The relevance of kinetic studies of photoelectrodes on such a short timescale is largely unexplored: see Schwarzburg and Willig (1997).

12.6 Modulation spectroscopies

12.6.1 Electrolyte electroreflectance spectroscopy

Electrolyte electroreflectance (EER) spectroscopy of semiconductors is based on the use of a transparent electrolyte contact to form a Schottky barrier in which the electric field perturbs the optical constants (*i.e.* the real and imaginary components of the complex dielectric function) of the solid. Under depletion conditions, the width of the space-charge region, and hence the electric field distribution, is determined by the applied DC potential. If a small square-wave or sinusoidal perturbation of the potential is superimposed on the DC potential, modulation of the optical constants by the AC field manifests itself by a modulation of the reflected light intensity. The change in optical properties can also be detected by transmission if the sample is thin enough (electrolyte electroabsorption spectroscopy: EEA). The spectra are normalised by dividing the modulated reflectance change ΔR by the 'DC' reflectance R to give the ratio $\Delta R/R$ (Hamnett, 1989; Hamnett *et al.*, 1992). The reflectivity changes occur when the photon energy corresponds to a critical electronic transition of the semiconductor band structure (a critical point in the joint density-of-states function). Under these conditions, the in-phase $(\Delta R/R)^{\text{ph}}$ and quadrature $(\Delta R/R)^{\text{qd}}$ components of $\Delta R/R$ can be measured using the lock-in technique. Under so-called 'low-field' conditions in the depletion region, the EER signal is given by (Aspnes, 1973)

$$\frac{\Delta R}{R} = \frac{2qN_D V_{\text{AC}}}{\epsilon_0 \epsilon_s} L(\hbar\omega) \quad (12.18)$$

where N_D is the donor concentration, V_{AC} is the fundamental harmonic component of the AC voltage applied across the depletion layer, $\epsilon_0 \epsilon_s$ is the static dielectric constant and $L(\hbar\omega)$ is the spectral line shape function (see below).

The theoretical treatment of EER lies outside the scope of this chapter. The interested reader is referred to the comprehensive reviews by Aspnes (1980) and Hamnett (1989). Under certain conditions, EER spectra are related to the third derivative of the complex dielectric function, and they can be described by a generalised line shape function first proposed by Aspnes (1973)

$$\frac{\Delta R}{R} = L(\hbar\omega) = \text{Re} \left[C e^{i\theta} (E - E_g + i\Gamma)^{-n} \right] \quad (12.19)$$

where E_g is the bandgap energy, Γ is a broadening function, θ is a phase-projection factor, n is a constant related to the nature of the critical point in the band structure

and C is a constant of proportionality. EER spectra can be fitted to the line function by non-linear regression. Initial values are conveniently derived using the 3-point method of Aspnes, which derives values of E_g , and Γ from the maxima and minima and crossing point in the EER spectrum. Γ can be related to compositional inhomogeneity and defect densities: single-crystal materials generally exhibit narrow EER spectra (small Γ), whereas polycrystalline materials give broader spectra with correspondingly large values of Γ .

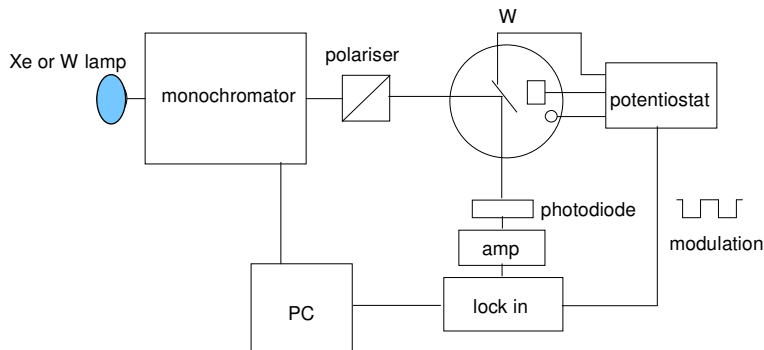


Figure 12.21 Experimental arrangement for electroreflectance spectroscopy.

Figure 12.21 shows the experimental arrangement for EER and EEA spectroscopy. By careful design and elimination of noise, $\Delta R/R$ values smaller than as 10^{-6} can be detected. For work in the visible, a tungsten lamp often gives better results than a xenon arc lamp unless the arc is stabilised. A polariser can be used to define the polarisation state of the incident radiation, although this is often omitted. The detector can either be a UV-enhanced silicon photodiode or a photomultiplier. It is important to minimise pick-up of the modulation signal by the diode since this gives a spurious constant response in the ΔR signal. The error is usually manifest as a wavelength-dependent offset. Since the constant ΔR error is divided by a varying R , the offset is most serious when R becomes small—typically at short wavelengths. It can be eliminated by suitable shielding and optimisation of the detector position. Since capacitive pickup increase linearly with frequency, it is advantageous to use low modulation frequencies wherever possible if high sensitivity is required.

For thin-film samples, measurements can be made using transmitted rather than reflected light. Figure 12.22 illustrates the use of electroabsorbance spectroscopy (EEA), showing how the EEA spectrum of an electrodeposited CdS/CdTe solar cell structure changes as a result of thermal annealing. The CdS layer is n -type, as is the as-deposited CdTe. Annealing at 415 C type-converts the deposited CdTe to form an

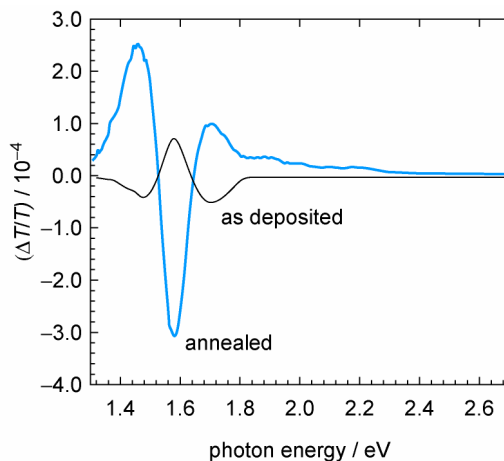


Figure 12.22 Electrolyte electroabsorption spectra for as-deposited and annealed electrodeposited films of CdTe on CdS/TCO/glass. Adapted from Duffy *et al.* (2000a).

n -CdS/ p -CdTe junction. The EEA spectra reveal that type-conversion is accompanied by a reduction in Γ and a shift in E_g to lower energies (Duffy *et al.*, 2000a).

EER has been used in combination with electrochemical and chemical etching to obtain compositional profiles through semiconductor devices such as $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ infrared detectors (Berlouis *et al.*, 1987 and 1990). The bandgap determined from the EER spectra is usually related to the composition by an empirical polynomial in x . This approach has been used by Hutton and Peter (1993) to study $\text{Ga}_x\text{Al}_{1-x}\text{As}$ samples prepared by MOCVD.

$\Delta R/R$ decreases and changes sign as the potential is scanned through the flatband potential. This property of the EER signal can be used to determine the flatband potential of photoelectrodes, especially in cases when unpinning of the energy band position interferes with a standard Mott–Schottky plot evaluation (Pujadas and Salvador, 1989; Tafalla *et al.*, 1989; Salvador *et al.*, 1991). The method has also been applied to determine the flatband potential of anodic oxides such as TiO_2 on titanium (Blackwood and Peter, 1990). It can also be used to follow the shift of the flatband position in response to surface treatment. If the surface of the semiconductor has a high density of fast surface states N_{ss} , the surface electron population can be modulated with the applied potential (non-negligible contribution of dN_{ss}/dV). As a result, a smaller fraction of the AC potential appears across the space-charge layer so that $\Delta R/R$ decreases (Abrantes *et al.*, 1987; Hamnett, 1989; Hutton *et al.*, 1994).

The electroreflectance effect described in the preceding section arises from a perturbation of the optical constants of the electrode by an applied electric field.

Potential-dependent reflectance changes at an electrode may also be a consequence of an electrode reaction that changes the absorption coefficient of a surface film or of the solution adjacent to the surface. The more general term ‘potential-modulated reflectance spectroscopy’ (PMR) is used to describe the experimental method in this case. The apparatus is the same as that used for EER, but the origin and characteristics of the PMR response are different (see, *e.g.*, Walker *et al.*, 1998).

12.6.2 Calorimetric measurements

In photocalorimetry, the relative temperature change of a photoactive electrode is measured as a function of the electrode potential under chopped monochromatic illumination (Fujishima *et al.*, 1977; Rappich and Dohrmann, 1989; Dohrmann and Schaaf, 1992; Dohrmann and Reck, 1998). Either pyroelectric or piezoelectric sensors or photoacoustic microphones are coupled to the back surface of the photoelectrode to monitor the temperature change produced by the transmitted heat wave. Alternatively, photothermal laser beam reflection at the front surface of the semiconductor/liquid junction can be utilised to probe the modulated temperature (Royce *et al.*, 1982). Irrespective of the detector scheme, which in modern studies frequently relies on easy-to-handle piezo films (*e.g.* polyvinylidene difluoride foil), photocalorimetry offers the opportunity to measure a variety of parameters that are relevant for energy-converting interfaces. The potential dependence of the photocurrent and the piezoelectric detector signal can be measured simultaneously by a lock-in technique. The characteristic curves obtained give access to the internal quantum efficiency of the photocurrent, the internal energy conversion efficiency of reactions, the Peltier heat of photoelectrochemical reactions, (which is related to the entropy change of the reaction) and the heat of transport.

Theoretical analysis starts from the energy conservation law and the fact that the power absorbed by the photoactive material is given by the product of the photocurrent and the photovoltage plus all the losses that appear as heat and can be measured via the sensor signal. It is assumed that luminescent light emission can be neglected. The heat losses occurring within an illuminated semiconductor/electrolyte interface are depicted schematically in Fig. 12.23. The sum of all heat loss processes ($-dQ/dt = -\dot{Q}$) shown in this figure adds up to

$$-\dot{Q} = \Phi_a - I_{\text{ph}} U_{\text{ph}} = \dot{N}_a \left\{ E_\lambda + \eta_a(E) \left[-qU_{\text{redox}} - E_F - T(\Delta S_{\text{et}} + \Delta S_{\text{ox}}) \right] \right\} \quad (12.20)$$

where $\dot{N}_a$ is the rate of photon absorption, E_λ is the photon energy, $\eta_a = \dot{N}_c / \dot{N}_a$ is the internal quantum efficiency, U_{redox} is the redox potential, ΔS_{et} and ΔS_{ox} are entropy

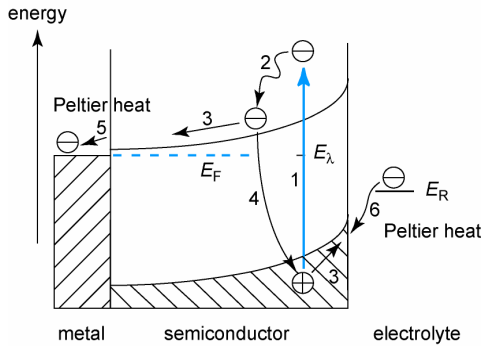


Figure 12.23 Photon energy input and heat losses for a photoelectrode/liquid junction. (1) Photonic energy input; (2) relaxation loss; (3) drift loss; (4) recombination loss; (5) liberation of Peltier heat at the back contact; (6) relaxation loss and liberation of Peltier heat at the electrolyte contact.

turnovers during electron transfer at the back contact and the oxidation process at the electrolyte interface, respectively, and E_F is the Fermi energy. Both entropy terms and resistive heat loss are included. No photocurrent flows at the flatband potential. Defining the Peltier heat Q_{PE} as the fraction of photon energy that cannot be converted into useful work

$$Q_{PE} = -T(\Delta S_{et} + \Delta S_{ox}) \quad (12.21)$$

the normalised quantity

$$L = \frac{P(U) - P(U_{fb})}{P(U_{fb})} = \frac{\eta_a}{E_\lambda} [q(U - U_{redox}) + Q_{PE}] \quad (12.22)$$

can be obtained. Here $P(U)$ is the calorimetric signal, which is proportional to the heat evolved. In photocalorimetry it is described by a characteristic potential dependence. It follows that the internal quantum efficiency can be obtained. The following linear function results (A = electrode surface area and ${}^0U = U_R - Q_{PE}/q$).

$$\frac{L}{i_{ph}} = \frac{A}{\Phi_a} (U - {}^0U) \quad (12.23)$$

with

$$\Phi_a = \frac{j_{ph}(U)E_\lambda}{F\eta_a(U)} \quad (12.24)$$

The plot of this function against potential crosses zero at a characteristic potential 0U . The function Φ_a , which is obtained from the reciprocal value of the slope, can be

used to calculate the internal quantum efficiency η_a . The Peltier heat Q_{PE} , which is accessible from the intersection of the straight line with the potential axis, deserves further theoretical and experimental study since it is related to, and influenced by, semiconductor electrode reactions.

Figure 12.24 shows a set-up for the measurements, including a photocalorimetric cell with 1 μm to 1 mm thick electrodes. The relative changes of the sensor signal (and hence the relative change of the internal quantum efficiency of the photocurrent) are evaluated as a function of U . Figure 12.25 is an example of such a measurement.

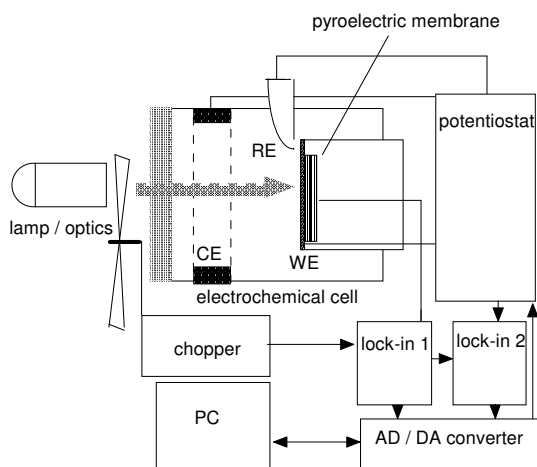


Figure 12.24 Experimental set-up for combined photoelectrochemical and photocalorimetric measurements.

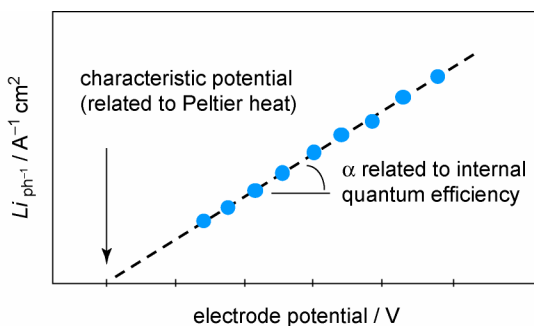


Figure 12.25 Example of plot of eq. 12.23 for the determination of the internal quantum efficiency (from the slope) and Peltier heat (from the intercept on the potential axis).

12.7 Frequency-resolved light modulation methods

12.7.1 Intensity-modulated photocurrent spectroscopy

Intensity-modulated photocurrent spectroscopy (IMPS) is used to derive information about photoelectrochemical processes by measuring the frequency-dependent magnitude and phase shift of the photocurrent generated by intensity-modulated light (Li and Peter, 1985 and 1986; Peat and Peter, 1986 and 1987; Peter, 1990a,b; Ponomarev and Peter, 1995; Peter *et al.*, 1997; Fermin *et al.*, 1999; Peter, 1999; Peter and Vanmaekelbergh, 1999). In principle, the intensity of the light can be modulated using a mechanical chopper, but it is more convenient to use either a light emitting diode (LED) or an acousto-optic modulator with a cw laser. Generally the AC-modulated illumination is superimposed on a much larger DC component that may be provided, if necessary, by a second source. Figure 12.26 shows a typical experimental arrangement using an LED.

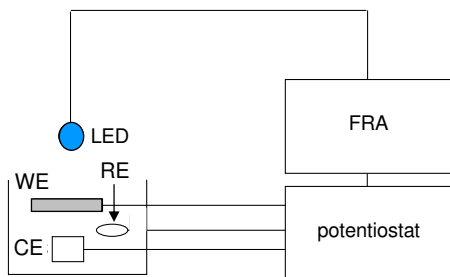


Figure 12.26 Experimental set-up for IMPS.

If an acousto-optic modulator is used, the reference signal for the frequency response analyser (FRA) should be provided by a fast photodiode that samples the incident light via a beam splitter. The reason for this is that the acoustic delay in the modulator gives rise to frequency-dependent phase shift between the driving voltage and the output light intensity. If an LED is used, the phase shift between the driving voltage and the light modulation is usually negligible at frequencies below 1 MHz, so that a beam splitter is not necessary. The bandwidth of the IMPS system is limited by potentiostat response, and for high-frequency measurements the cell design should be optimised by elimination of high-resistance reference electrodes and frits between compartments. Commercial potentiostats, including those developed for EIS measurements, may not be suitable for IMPS because the phase shift and attenuation may be unacceptable. This is not a problem in EIS measurements since the applied AC

voltage is measured across the cell. The safest approach to evaluate the phase error is to construct a dummy cell consisting of a fast photodiode and a series resistance. Most potentiostat/cell combinations suffer from gain peaking at high frequencies, and this may manifest itself in the high-frequency IMPS response as a large deviation from the expected intercept at the origin.

Even in the absence of limitations due to the potentiostat, the IMPS response at high frequencies is attenuated due to the RC time constant of the system arising from the series combination of the electrolyte and ohmic contact resistance with the electrode capacitance. For low-doped semiconductors under depletion conditions with good ohmic contacts, the RC time constant is short ($<10^{-7}$ s). Poor ohmic contacts (a common problem for p -type semiconductors) can have series resistances of several hundred ohms, which causes substantial RC attenuation at high frequencies. Similarly, highly doped semiconductors, anodic films and porous nanocrystalline electrodes can have high capacitances, leading to an increase in RC attenuation. It is therefore advisable to determine the RC time constant separately by EIS wherever possible.

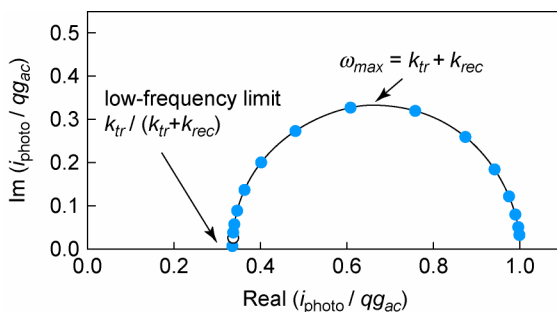


Figure 12.27 Schematic IMPS response for a single-crystal photoelectrode (the RC attenuation at high frequencies is not shown).

Figure 12.27 shows a schematic IMPS response for a monocrystalline semiconductor electrode. It is easy to confuse IMPS plots with EIS plots since both contain semicircles. However the quantity displayed in an IMPS plot is not an impedance or an admittance: it is the dimensionless transfer function corresponding to the ratio of the electron flux to the photon flux. The interpretation of the phase relationship between photocurrent and illumination requires some care. A response in the first upper quadrant indicates that the photocurrent ‘leads’ the illumination. A response in the lower quadrant indicates that the photocurrent lags behind the illumination. In the schematic response shown in Fig. 12.27, the low-frequency response in the upper quadrant of the complex plane arises from surface

recombination. It is not immediately evident why the photocurrent should appear to lead the illumination. The effect arises from the flux of *majority* carriers into surface states associated with recombination. The majority-carrier flux lags behind the photo-generated minority-carrier flux, but since the carriers have the opposite sign, an additional phase shift of 180° occurs. This is explained for an *n*-type semiconductor by the vector diagrams in Fig. 12.28.

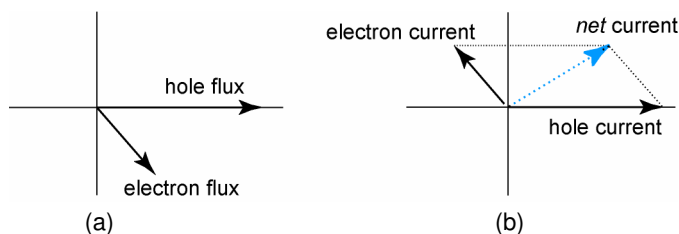


Figure 12.28 Vector diagrams showing (a) hole and electron fluxes and (b) corresponding currents for the IMPS response of an *n*-type semiconductor.

Analysis of the IMPS response gives information about the competition between charge-transfer and surface recombination, which are described by the rate constants k_{ct} and k_{rec} respectively (Peter *et al.*, 1997; Peter, 1999; Peter and Vanmaekelbergh, 1999). The low-frequency intercept on the normalised IMPS plot is given by the ratio $k_{\text{ct}}/(k_{\text{ct}} + k_{\text{rec}})$. If the RC time constant is much smaller than $(k_{\text{ct}} + k_{\text{rec}})^{-1}$, the IMPS plot should pass through a maximum at an angular frequency equal to $2\pi f = (k_{\text{ct}} + k_{\text{rec}})$ and cross the real axis at a value corresponding to the IPCE in the absence of surface recombination. The frequency of the minimum of the RC semicircle in the lower quadrant is given by $f_{\text{RC}} = 1/2\pi RC$.

A good example of the application of IMPS is illustrated in Fig. 12.29, which shows IMPS plots for *p*-InP in acidic solution (Ponomarev and Peter, 1995). The photoelectrochemical reaction is the evolution of hydrogen. The family of plots as a function of electrode potential shows how the low-frequency intercept moves towards the origin as the band bending is reduced and recombination becomes faster due to the increase in majority carrier (holes) concentration at the surface. Analysis of the semicircles gives values of k_{ct} and k_{rec} as a function of electrode potential. In the case of nanocrystalline electrodes, the IMPS response is located mainly in the lower quadrant, and at low light intensities, it extends to very low frequencies: an example for dye-sensitised nanocrystalline TiO_2 is shown in Fig. 12.30. This reflects the fact that photoinjected electrons appear to be collected by slow diffusion, giving rise to a frequency-dependent phase lag in the photocurrent. In fact the transport of free electrons in the conduction band of the nanocrystalline oxide is much faster, and the

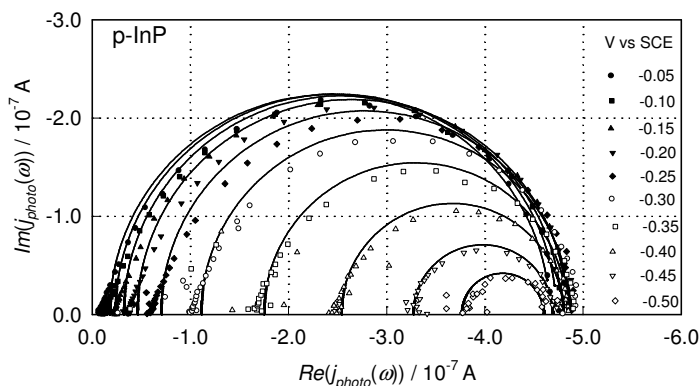


Figure 12.29 IMPS plots for *p*-InP in H₂SO₄ as a function of electrode potential. Adapted from Ponomarev and Peter (1995).

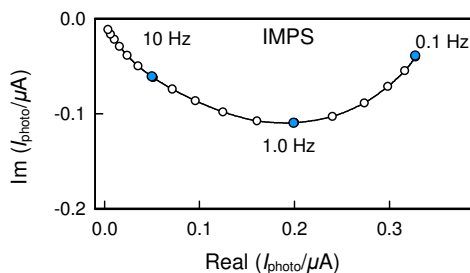


Figure 12.30 Typical IMPS response for a dye-sensitised nanocrystalline cell, showing response in the lower quadrant due to the phase lag associated with electron diffusion.

low values of the apparent electron diffusion coefficient are determined by trapping/detrapping processes (Peter, 2007). If electrons are generated at the interface furthest from the substrate electrode, the transit time manifests itself as a phase lag that increases with frequency, causing the IMPS plot to spiral through all four quadrants before reaching the origin (Vanmaekelbergh *et al.*, 1996; Dloczik *et al.*, 1997; Peter and Vanmaekelbergh, 1999). In this case it is useful to use Bode plots to display the magnitude and phase angle of the IMPS response. Dloczik *et al.* (1997) and Peter and Vanmaekelbergh (1999) give further details.

The IMPS plots can be fitted using the following analytical solution of the continuity equation, which describes the generation, transport and back reaction of electrons

$$\frac{\partial n}{\partial t} = \alpha I_0 e^{-\alpha x} + D_e \frac{\partial^2 n}{\partial x^2} - \frac{n - n_0}{\tau_e} \quad (12.25)$$

where α is the absorption coefficient, I_0 is the photon flux, D_e is the electron diffusion coefficient, n is the electron density under illumination, n_0 is the equilibrium (dark) electron density and τ_e is the electron lifetime.

12.7.2 Intensity-modulated photovoltage spectroscopy

The basic measurement technique for intensity-modulated photovoltage spectroscopy (IMVS) is the same as for IMPS. In principle, IMVS measurements can be made for any constant current condition, but in practice it is usual to make measurements under conditions where the net current is zero. In the case of a photoelectrochemical solar cell, this corresponds to the open-circuit condition, and a high impedance voltage amplifier is used to ensure that a negligible current is drawn from the illuminated device. The output of the voltage amplifier is fed to the FRA, and the remainder of the set up is the same as for IMPS (*cf.* Fig. 12.26).

In a conventional solid-state photovoltaic cell or a semiconductor/electrolyte junction, the photovoltage is related to the densities of free electrons and holes. These in turn define the quasi-Fermi levels nE_F and pE_F . The photovoltage is given by

$$qV_{\text{photo}} = nE_F - pE_F \quad (12.26)$$

The relationship between light intensity and photovoltage is generally non-linear, but the response can be linearised for sufficiently small modulation amplitudes. In practice, the modulation is set to give AC photovoltages of the order of a few mV. IMVS has been used mainly to study dye-sensitised nanocrystalline solar cells (Schlichthörl *et al.*, 1997; Peter and Wijayantha, 1999; Schlichthörl *et al.*, 1999; Fisher *et al.*, 2000). At open circuit, photoinjected electrons back-react with I_3^- ions in the electrolyte, and the decay of the photovoltage is related to the electron lifetime.

Figure 12.31 illustrates a typical IMVS response for a nanocrystalline dye-sensitised solar cell. The frequency $f_{\min}$ of the minimum in the semicircular complex plane plot is related to the electron lifetime by $\tau_e = 1/2\pi f_{\min}$. Again, the apparent electron lifetime is determined by the relaxation of the population of trapped electrons, and the free electron lifetime can only be found by modelling the influence of trapping/detrapping (Peter, 2007). The density of electron traps can be found using PEIS or by the charge extraction technique (Duffy *et al.*, 2000b; Bailes *et al.*, 2005), which involves switching the dye-sensitised cell from open circuit to short circuit to extract the trapped electrons.

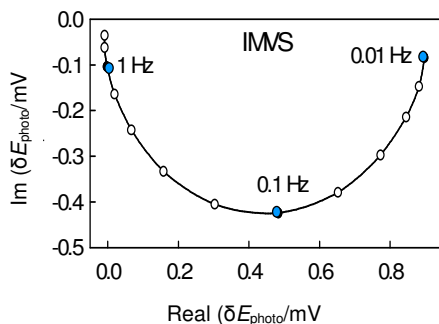


Figure 12.31 Typical IMVS response of a dye-sensitised nanocrystalline cell.

12.7.3 Light-modulated microwave reflectivity

The interpretation of IMPS data relies on the competition between charge transfer and recombination to give a semicircle that can be analysed to obtain k_{ct} and k_{rec} . It follows that IMPS provides no information if recombination is absent. Surface recombination usually becomes negligible at potentials sufficiently far from the flatband potential, where a plateau is seen in the photocurrent–potential plot. IMPS plots measured in the plateau region do not exhibit a semicircle in the upper quadrant; only the lower RC semicircle is seen. Light-modulated microwave reflectance spectroscopy (LMMRS), on the other hand, can provide information about k_{ct} even when $k_{rec} = 0$ (Schlichthörl *et al.*, 1995; Peter and Vanmaekelbergh, 1999). The reason for this is that microwave reflectivity detects the decay of photogenerated free charge carriers that are located at the surface, regardless of whether they are transferred across the interface or recombine with majority carriers. This is demonstrated by Fig. 12.32, which contrasts the calculated photocurrent and microwave responses for chopped illumination in the plateau photocurrent region.

Figure 12.33 illustrates the set-up for LMMRS. The frequency response analyser replaces the single frequency lock-in amplifier used in the potential and light modulated microwave measurements described in Section 12.3. LMMRS detects the frequency-dependent modulation of the microwave reflectivity ΔR_M associated with the photogenerated minority carriers. This concentration decays by interfacial charge transfer (k_{ct}) and recombination (k_{rec}). The LMMRS response is therefore a semicircle with a characteristic frequency $\omega_{min} = (k_{ct} + k_{rec})$. The low-frequency intercept of the LMMRS plot is given by (Schlichthörl *et al.*, 1995)

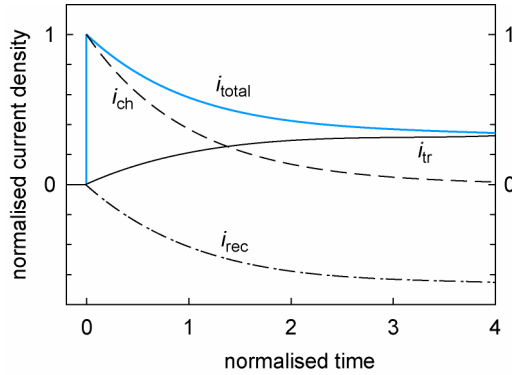


Figure 12.32 Deconvolution of the currents at a semiconductor electrode for step-function illumination, showing the charging current i_{ch} , the recombination current i_{rec} and the charge-transfer current i_{ct} . Note that i_{ct} depends on the density of photogenerated carriers at the interface, which is detected by LMMR, *i.e.* the microwave signal follows the i_{ct} curve.

$$\text{Re}(\Delta R_M) = \frac{S q j_o}{k_{\text{ct}} + k_{\text{rec}}} \quad (12.27)$$

where S is the sensitivity factor and j_o is the absorbed photon flux. The high-frequency LMMRS intercept is zero. If S is known, k_{ct} and k_{rec} can be obtained using ω_{min} and the low-frequency intercept.

This behaviour contrasts with the IMPS response, where the high-frequency intercept is $q j_o$ and the low-frequency intercept is given by

$$\text{Re}(i_{\text{photo}}) = \frac{q j_o k_{\text{ct}}}{k_{\text{ct}} + k_{\text{rec}}} \quad (12.28)$$

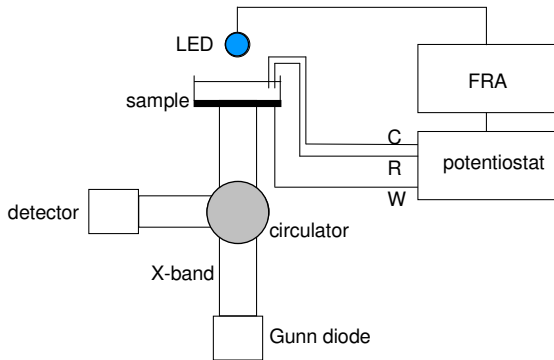


Figure 12.33 Experimental set-up for LMMRS.

It follows that LMMRS still gives a semicircle when $k_{\text{ct}} \rightarrow 0$ at high band bending. By contrast in the case of IMPS, the diameter of the semicircle contracts to zero at high band bending (in terms of the normalised IMPS response, i_{photo}/qj_0 is unity). The contraction in the diameter of the IMPS semicircle can be seen in the data for $p\text{-InP}$ shown in Fig. 12.30. This means that LMMRS be used to obtain k_{ct} over a wide potential range, whereas the IMPS analysis is restricted to the photocurrent onset region where appreciable recombination occurs.

LMMRS has not been used extensively. This probably reflects the fact that few groups are actively using microwave techniques at present. The main limitations of the method are associated with the need to use low-doped samples in order to obtain sufficient sensitivity. Figure 12.34 shows LMMRS data obtained for $p\text{-Si}$ in fluoride solution. The photoelectrochemical reaction in this case is hydrogen evolution, and analysis of the IMPS and LMMRS data for this system have confirmed that the two methods give consistent values for the electron-transfer rate constant, demonstrating the validity of the LMMRS approach. The important difference between LMMRS and IMPS is that LMMRS still provides information when there is no recombination. By contrast, IMPS provides no information in this region.

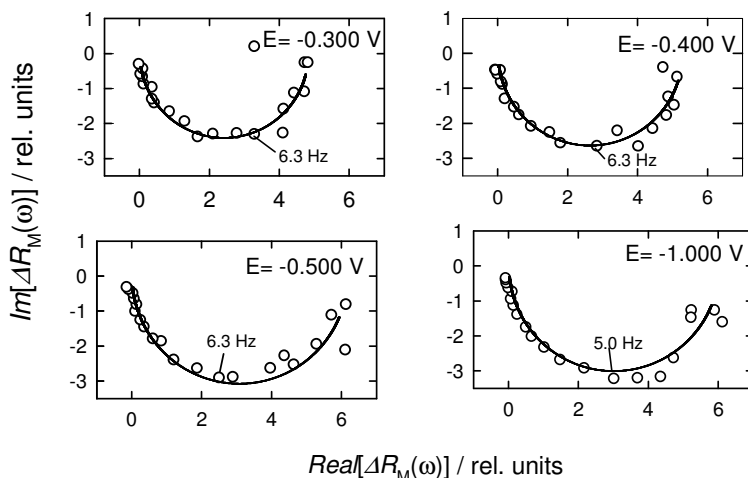


Figure 12.34 LMMRS response of $p\text{-Si}$ in HF, showing that the semicircular response persists at negative potentials that are in the photocurrent saturation region. Note that the high-frequency intercepts in the plots are at zero. For further details, see Schlichthörl *et al.* (1995).

12.8 Imaging techniques

If, instead of measuring integral parameters of an energy-converting interface, a spatially resolved image is produced of a relevant quantity such as photocurrent, photopotential or microwave conductivity, luminescence or electroreflectance, significantly more information is available. Such a spatially-resolved image of a semiconductor interface typically shows patterns determined by inhomogeneities of the material or surface preparation. If photoelectrochemical reactions are allowed to proceed, it can be observed where they are best catalysed or where photocurrents tend to concentrate. By surface-modifying well-defined areas within these images, the effect of intentional changes on the overall performance of the system can be determined easily and quantitatively in comparison with untreated areas. For example, by projecting a gradient of light intensity onto a semiconductor electrode for a longer period, information on light intensity-dependent photodegradation can easily be obtained in a single experiment (see Fig. 12.37b for an experimental example).

Figure 12.35 shows a schematic set-up for imaging electrochemical quantities such as photocurrents or electroreflectance (Chaparro *et al.*, 1997) and Fig. 12.37a

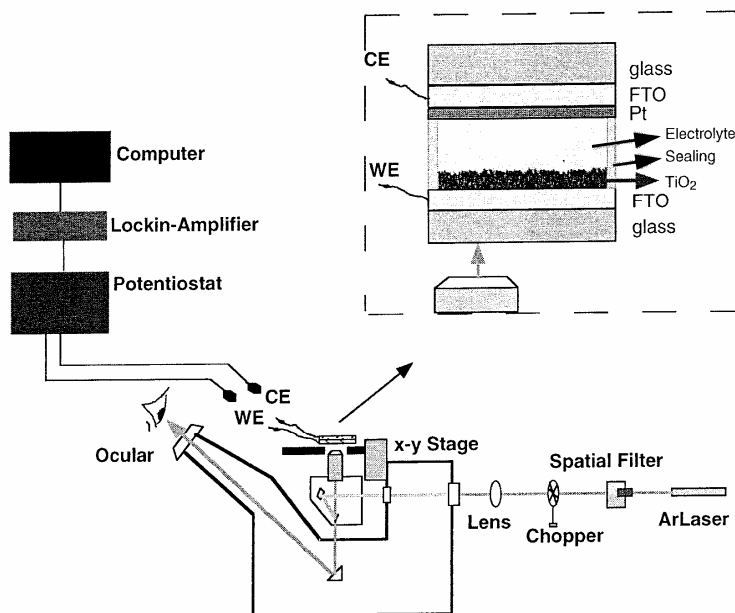


Figure 12.35 Scanning microscope for semiconductor characterisation (SMSC). The scanning of the laser spot is indicated in the insert with a dye-sensitised nanocrystalline cell.

presents an experimental measurement. Figure 12.13 shows a set-up for producing microwave conductivity images and Fig. 12.37c provides a measured image.

Infrared thermography is a well-established and widely used technique for the study of the distribution of temperature over solid interfaces. Thermographic images of energy-converting interfaces may give information on local heat sources, but also on different reflection properties of materials. A technique that has been especially developed for energy-converting interfaces consists in periodically modulating the incoming photon energy or the photocurrent by varying the working resistance of the solar device via a relay (lock-in thermal imaging) (Rappich *et al.*, 1998). A periodic heat emission is measured which is actually related to energy conversion with filtered-out contributions of stationary thermal emission and infrared reflection. Figure 12.36 shows the experimental set-up, and Fig. 12.37d experimental results.

The energy conversion efficiency η can readily be obtained from the temperatures T_{IR} and T_{oc} , measured under load and under open circuit respectively, in relation to the ambient temperature T_o and independent of the photon flux.

$$\eta = \frac{T_{\text{oc}} - T_{\text{IR}}}{T_{\text{IR}} - T_o} \quad (12.29)$$

The internal quantum efficiency η_{abs} can be deduced from

$$\eta_{\text{abs}} = \frac{\eta h\nu}{q\Delta U_{\text{photo}}} \quad (12.30)$$

where ΔU_{photo} is the photopotential.

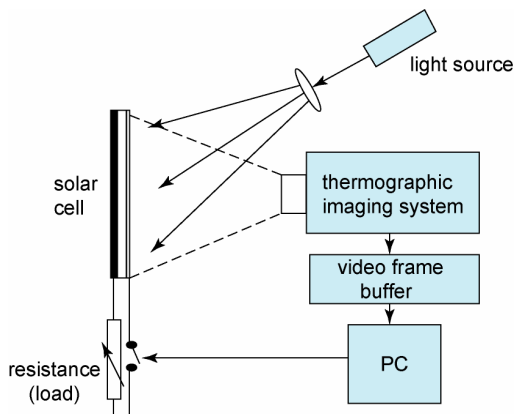


Figure 12.36 Set-up for thermographic technique for the generation of images measuring spatially-resolved energy conversion efficiencies.

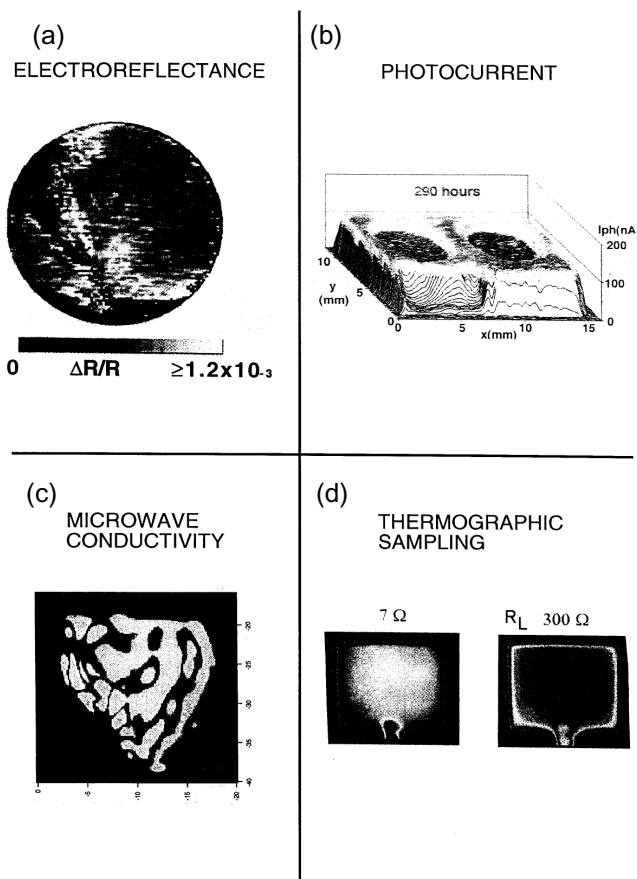


Figure 12.37 Scanning images. (a) EER image of inhomogeneously doped RuS_2 crystal (Chaparro *et al.*, 1997). (b) Photocurrent image of dye sensitised nanocrystalline TiO_2 cell after illumination for 290 hours with solar simulator light through two round openings. (c) Microwave photoconductivity image of natural FeS_2 crystal. (d) Thermographic sampling images of silicon solar cell for two different load resistances.

A periodic change of infrared emission due to periodic energy conversion is thus achieved for every point of the image, which can be monitored by sampling techniques. A 20–50 fold increase in sensitivity is achieved with respect to ordinary infrared imaging, allowing visualisation of surface areas where the photocurrents actually pass and participate in energy conversion. By observing the thermal properties of such an interface, the energy output can be determined for any point of the picture, providing detailed information on the operation of the device.

12.9 *In-situ* X-ray analysis and EXAFS

Photoelectrochemical mechanisms may be characterised by potential-dependent structural changes of the photoactive interfaces. These may include stoichiometric changes (*e.g.* intercalation or excalation of ionic species), phase changes or dynamic molecular changes of photocatalytic species. In all these cases, time-dependent structural information is desirable. This may be accomplished with *in-situ* X-ray and EXAFS (X-ray absorption fine structure) techniques. For such measurements, the electrochemical cell is integrated into a 'Plexiglass' body covered with Capton layers that are penetrated by the X-rays from the diffractometer source or the synchrotron (EXAFS), which are incident at a low grazing angle, as shown in Fig. 12.38.

Schubert *et al.* (1996) undertook *in-situ* X-ray studies to determine the origin of H_2O_2 production during oxygen reduction at transition-metal cluster materials. They observed that H_2O_2 generation increased from an originally very low level due to oxidation of the material and excalation of inserted metal species from inside of the material. Alonso-Vante and Borthen (1997) performed *in-situ* EXAFS studies to investigate whether a RuMo-cluster catalyst changes its structure during oxygen reduction. They found that the Ru–Ru distance changes, but not the Mo–Mo distance.

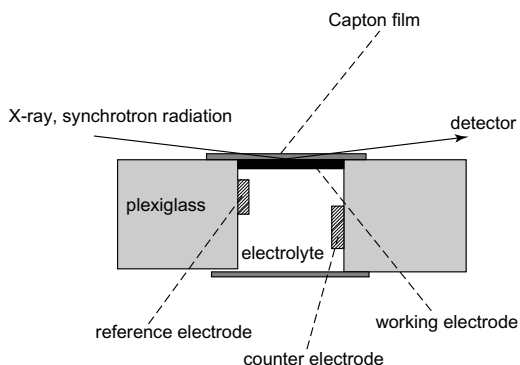


Figure 12.38 Cell for *in-situ* X-ray and EXAFS studies of interfacial electrochemical processes.

12.10 Differential mass spectrometry (DEMS)

For fuel-generating photoelectrochemical devices, it is desirable to determine chemical products dynamically *in situ* during potential variations. This is possible when mass spectroscopy is coupled to electrochemical experiments via specific

membranes that are permeable to volatile chemicals but which separate the electrolyte from a vacuum chamber linked to the mass spectrometer (Bittins-Cattaneo *et al.*, 1991; Schmidt *et al.*, 1996). Various arrangements have been developed and applied. Critical factors are the construction of the electrode and the transport mechanism of chemicals to the semipermeable membrane. A DEMS set-up is very useful to investigate and improve photocatalytic properties, since the photocurrents can be correlated with detection of photogenerated products, which can be quantitatively measured.

To drive the volatile products directly from the electrode surface via a suitable inlet system into the vacuum chamber of the mass spectrometer, a plain gas-permeable membrane (*e.g.* PTFE or polyethylene) on which the electrode material is deposited by sputtering or vacuum evaporation is usually used. Alternatively, the material can be deposited onto a metal gauze that is fixed close to the gas-permeable membrane. DEMS cell constructions such as that shown in Fig. 12.39 have been described that allow the use of massive electrodes, which are more easily available.

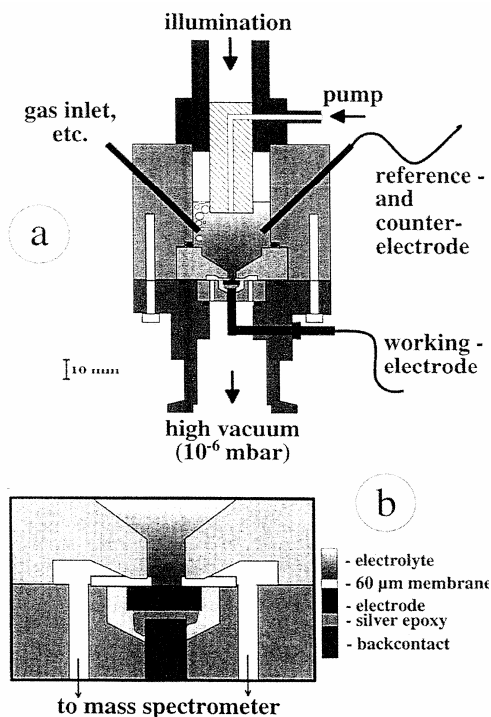


Figure 12.39 DEMS cell for massive photoelectrodes (Bogdanoff *et al.*, 1998).

From the upper part of the electrochemical cell, a ring of a gas-permeable membrane is pressed on the electrode. This ring separates the high vacuum from the electrolyte and serves as the specialised inlet system. Volatile products generated at the photoelectrode can diffuse sideways through the membrane into the mass spectrometer, where they are analysed. With this cell, photoassisted electrochemical reactions can be studied even at relatively high current densities and in the presence of significant gas evolution. An example of a system studied under such conditions is the photocorrosion of *p*-type InP single crystals (Bogdanoff *et al.*, 1998).

12.11 Combination of electrochemistry with vacuum spectroscopy

Ultra-high vacuum surface science techniques use electrons or ions as probes that interact with matter sufficiently strongly that surface-specific information is obtained. Typically, a combination of techniques is used to characterise a surface as completely as possible.

Table 12.1 List of vacuum techniques used to characterise semiconductor surfaces.

Technique	Particle/photons in/out	Information depth/nm	Type of information
UV photoelectron spectroscopy (UPS)	UV/electrons	0.5–20	electronic structure of valence band interfacial energetics
X-ray photoelectron spectroscopy (XPS)	X-rays/electrons	1–3	elemental composition valence states of elements
Electron loss spectroscopy (ELS, HREELS)	electrons/same electrons	0.5–2	electronic and vibronic excitation
Auger electron spectroscopy (AES, SAM)	electrons/Auger electrons	1–2	elemental composition valence states of elements
Low energy electron diffraction (LEED)	electrons/same electrons	0.5–1	geometric surface structure
Secondary ion mass spectrometry (SIMS)	ion/ions	5	elemental composition
Ion scattering spectroscopy (ISS, LEISS).	ions/same ions	0.3	elemental composition and structural information
Inverse photoemission (IPE, BIS)	electrons/photons	0.5–3	electronic structure of conduction band

As Table 12.1 shows, a wide range of scientific information is made accessible, which has attracted the attention of groups interested in solid-state and solid-liquid solar energy-converting junctions.

While the deposition of solid films onto semiconducting interfaces for the purpose of forming an energy-converting junction is straightforward, the modelling of solid/liquid junctions requires specific strategies and tools because of the liquid state of the electrolyte, which cannot exist in the vacuum. Figure 12.40 shows a set-up for performing model experiments on semiconductor/electrolyte interfaces.

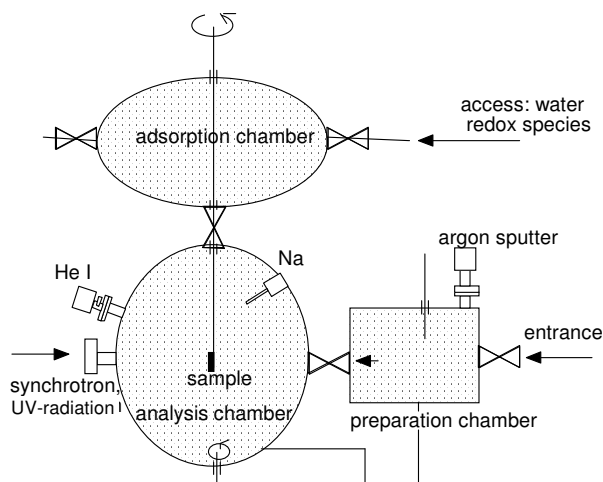


Figure 12.40 Instrumentation for combined electrochemical/UHV experiments.

The main analyser chamber contains a spectrometer and ports for different excitation sources. The preparation chamber is needed for sample preparation (*e.g.* cleavage). The electrolyte components are allowed to react with the interface in the adsorption chamber, where temperature control is used to stabilise the interface-adsorbate interaction. Water, halogen and alkali species are allowed to interact with electrode material to investigate structure and potential distribution of the electrochemical double layer (Sass, 1983; Bange *et al.*, 1987; Sass *et al.*, 1990). Jaegermann (1996) gives a comprehensive review of the semiconductor/electrolyte interface within the vacuum science approach.

Experimentation with vacuum photoelectron or ion spectroscopy is quite sophisticated and in no way a routine procedure, and many open questions have to be answered. In principle it is assumed that fundamental interactions can be simulated in

model experiments that approach real conditions. However, real electrolytes have a more complex composition, so that further studies are needed. At semiconductor electrodes, charge transfer and the interfacial potential drop lead to formation of an extended space-charge layer. Surface dipole changes may shift the position of the energy bands. The corresponding changes of electron affinity or ionisation potential can be measured with photoelectron spectroscopy. Also intrinsic and extrinsic surface states induced by the adsorbed phase can be identified by additional emission intensity in the valence-band region and by shifts of electrostatic potentials. A drawback is that the sensitivity for a direct spectroscopy of surface species is typically restricted to about 1% of a monolayer, whereas changes in surface potentials resulting in band bending may already be induced by less than 0.1% of a monolayer. In principle, fundamental interactions of electrolyte species with well-defined semiconductors can be studied effectively, and quite complex solid-state electrolyte interfaces can be modelled by co-adsorption of several electrolyte species. It is useful to combine these experiments with *ex-situ* studies and electrochemical experiments on the same interfaces.

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APPENDIX I

Fundamental Constants

Quantity	Symbol	Value
Speed of light in vacuum	c	$2.998 \times 10^8 \text{ m s}^{-1}$
Planck constant	h	$6.626 \times 10^{-34} \text{ J s}$
Faraday constant	F	$9.6485 \times 10^4 \text{ C mol}^{-1}$
Boltzmann constant	k	$1.3807 \times 10^{-23} \text{ J K}^{-1}$
Permittivity of vacuum	ϵ_0	$8.854 \times 10^{-12} \text{ F}^{-1} \text{ m}^{-1}$
Unsigned charge on an electron	q	$1.602 \times 10^{-19} \text{ C}$
Gas constant	R	$8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$

APPENDIX II

Useful Quantities and Conversion Factors

$$1 \text{ eV} = 1.6022 \times 10^{-19} \text{ J} = 96.488 \text{ kJ mol}^{-1} = 8065.6 \text{ cm}^{-1} = 2.4180 \times 10^{14} \text{ Hz}$$

$$1 \text{ cm}^{-1} = 1.9864 \times 10^{-23} \text{ J} = 11.963 \text{ J mol}^{-1} = 0.12398 \text{ meV} = 2.9979 \times 10^{10} \text{ Hz}$$

$$1239.8/(\lambda/\text{nm}) = E/\text{eV}$$

$$kT \text{ at } 298.15 \text{ K} = 0.02569 \text{ eV}$$

$$kT/q \text{ at } 298.15 \text{ K} = 0.02569 \text{ V}$$

$$(\ln 10)kT/q \text{ at } 298.15 \text{ K} = 0.05915 \text{ V}$$

$$h/2\pi = 6.582 \times 10^{-16} \text{ eV s}$$

$$1 \text{ kWh} = 3.6 \times 10^6 \text{ J}$$

APPENDIX III

List of Symbols

Symbol	Preferred Unit	Description
A		electron acceptor
A		absorptance
c_i	mol dm^{-3}	molar concentration of species i
C	$\mu\text{F cm}^{-2}$	capacitance
C_{H}	$\mu\text{F cm}^{-2}$	Helmholtz layer capacitance (per unit area)
C_{scl}	$\mu\text{F cm}^{-2}$	space-charge layer capacitance (per unit area)
D		electron donor
$D(E)$	$\text{cm}^{-3} \text{eV}^{-1}$	density of electronic states of energy E
D_i	$\text{cm}^2 \text{s}^{-1}$	diffusion coefficient of species i
$D_{e,h}$	$\text{cm}^2 \text{s}^{-1}$	diffusion coefficient of electron or hole
E	eV molecule^{-1} or kJ mol^{-1}	internal energy
$E_{\text{c}}, E_{\text{v}}$	eV	conduction or valence band-edge energy
E_{F}	eV	Fermi level
$E_{\text{F},p}, E_{\text{F},n}$	eV	quasi-Fermi level of holes or electrons
E_{g}	eV molecule^{-1} or kJ mol^{-1}	band-gap energy or minimum energy for electronic excitation
E_{o}^{s}	W m^{-2}	incident solar irradiance
E_{λ}	$\text{W m}^{-2} \text{nm}^{-1}$	spectral irradiance per unit wavelength
$\mathcal{E}$	V m^{-1}	electric field strength
f	Hz	frequency
f_i	kJ m^{-2}	force constant of i th vibrational mode
G	eV molecule^{-1} or kJ mol^{-1}	Gibbs free energy
G	$\text{cm}^{-3} \text{s}^{-1}$ or $\text{m}^{-3} \text{s}^{-1}$	volume generation rate (of charge carriers)
H	eV molecule^{-1} or kJ mol^{-1}	enthalpy
H_{RP}	eV molecule^{-1}	electronic coupling matrix element between reactant (R) and product (P) states
i	mA cm^{-2}	current density
i_{ph}	mA cm^{-2}	photocurrent density

Symbol	Preferred Unit	Description
i_j	mA cm^{-2}	junction (dark) current density
i_o	mA cm^{-2}	reverse-bias saturation current density
I	A	current
j_{ph}	$\text{photons m}^{-2} \text{s}^{-1}$	flux of photons with $\lambda \leq \lambda_g$
j_o	$\text{photons m}^{-2} \text{s}^{-1}$	incident photon flux
j_s^o	$\text{photons m}^{-2} \text{s}^{-1}$	incident solar photon flux of all wavelengths
j_λ	$\text{photons m}^{-2} \text{s}^{-1}$	spectral photon flux with respect to wavelength
k		momentum vector
k_{ct}	cm s^{-1}	heterogeneous rate constant for charge transfer at an electrode
k_{nr}	s^{-1}	rate constant for nonradiative decay
k_r	s^{-1}	rate constant for radiative decay
L		litre
$L_{e,h}$	m	minority-carrier diffusion length of an electron or hole
m_e^*, m_h^*	kg	effective mass of an electron or hole
n	cm^{-3} or m^{-3}	electron concentration in the conduction band of a semiconductor
n_o	cm^{-3} or m^{-3}	equilibrium electron concentration
n_s	cm^{-3} or m^{-3}	surface electron concentration
n_r		refractive index
N_A, N_D	cm^{-3} or m^{-3}	density of acceptor or donor impurities
N_c, N_v	cm^{-3} or m^{-3}	effective density of states in conduction or valence band
p	atm or Pa	pressure
p	cm^{-3} or m^{-3}	hole concentration in the valence band of a semiconductor
p^o	cm^{-3} or m^{-3}	equilibrium hole concentration
P	W cm^{-2} or W m^{-2}	power density
Q_{sc}	C cm^{-2} or C m^{-2}	charge in space-charge layer per unit surface area
r_λ		reflectivity at wavelength λ
R	Ω	resistance

Symbol	Preferred Unit	Description
R	$\text{cm}^{-3} \text{s}^{-1}$ or $\text{m}^{-3} \text{s}^{-1}$	volume recombination rate (of charge carriers)
$R_{\square}$	$\Omega \text{ square}^{-1}$	sheet resistance
R_{L}	Ω	load resistance
S	cm s^{-1} or m s^{-1}	surface recombination rate
scl		(superscript or subscript) space-charge layer
t	s	time
t	eV molecule^{-1}	nearest-neighbour hopping integral
T	K	absolute temperature
T_{DA}	eV molecule^{-1}	transfer integral between donor (D) and acceptor (A) states
u		Bloch function
$u_{\text{e}}, u_{\text{h}}$	$\text{cm}^2 \text{s}^{-1} \text{V}^{-1}$	electron or hole mobility
$u_{\mathcal{E}}$	cm s^{-1}	drift speed in electric field strength $\mathcal{E}$
U	kJ or eV	potential energy
$U_{\text{Ox, Rd}}$	V vs. ref.	electrode potential for the reaction $\text{Ox} + ne^{-} \rightleftharpoons \text{Rd}$ vs. reference electrode
U°	V vs. ref	standard electrode potential (based on activities)
$U^{\circ'}$	V vs. ref	formal electrode potential (based on concentrations)
U_{fb}	V vs. ref	flatband potential
V	m^3	volume
V	V	voltage
V_{b}	V	band-bending potential
V_{bi}	V	built-in potential
V_{b}°	V	equilibrium band-bending potential
V_{th}	V	thermal voltage $(\beta)kT/q$ ($= 0.02569 \text{ V}$ for $\beta = 1$ and 25 C)
w	cm or m	width of space-charge layer
Y	S cm^2	admittance
Z	$\Omega \text{ cm}^{-2}$	impedance (per unit area)
α	cm^{-1} or m^{-1}	optical absorption coefficient (absorptivity)
α_{λ}	cm^{-1} or m^{-1}	optical absorption coefficient at wavelength λ
β	cm^{-1} or m^{-1}	attenuation coefficient

Symbol	Preferred Unit	Description
β		diode ideality factor
ϵ	$\text{M}^{-1} \text{cm}^{-1}$	molar extinction coefficient
ϵ_{op}		optical dielectric constant ($\epsilon_{\text{op}} = n_r^2$)
ϵ_s		static dielectric constant
η	V	overpotential
η		conversion efficiency
η_{mp}		maximum-power conversion efficiency
κ		quantum mechanical transmission coefficient
λ	kJ or eV	reorganisation energy
λ	nm	wavelength
λ_g	nm	wavelength corresponding to bandgap energy
μ_i	eV molecule^{-1}	chemical potential of species i
$\tilde{\mu}_i$	eV molecule^{-1}	electrochemical potential of species i
$\tilde{\mu}_{\text{F}}$ or E_{F}	eV	Fermi level
$\tilde{\mu}_{\text{e}}, \tilde{\mu}_{\text{h}}$	eV	quasi-Fermi level of an electron or hole
ν	Hz	frequency
ν_{n}	Hz	rate of passage through transition state
$\bar{\nu}$	cm^{-1}	wavenumber
ξ		photonic efficiency
ξ_{rel}		relative photonic efficiency
ρ	C cm^{-3}	space-charge density
ρ	$\Omega \text{ cm}$	electrical resistivity
ϕ	V	inner electric potential (Galvani potential)
ϕ		quantum yield
ϕ_{b}	V	barrier potential
$\Delta\phi_{\text{scl}}$	V	space-charge layer potential drop
Φ	eV	work function
χ	V	surface (dipole) electric potential
ψ	V	outer (Volta) electric potential
ψ		wavefunction
ω	rad s^{-1}	angular frequency

APPENDIX IV

Acronyms and Abbreviations

AES	Auger electron spectroscopy
ALD	atomic layer deposition
AM	air mass
AOT	advanced oxidation technology
ATR	attenuated total internal reflection
BT(E)X	mixture of benzene, toluene, (ethylbenzene) and xylenes
BHJ	bulk heterojunction
cb	(as a superscript or subscript) conduction band
CBM	conduction-band minimum
CCD	charge-coupled [silicon] detector
CE	counter electrode
COD	chemical oxygen demand
ct	charge transfer
CVD	chemical vapour deposition
CZ	Czochralski (method of crystal growth)
DEMS	differential mass spectrometry
Dk	(as a superscript or subscript) in the dark
DSSC	dye-sensitised solar cell
EDX	energy-dispersive X-ray emission
EEA	electrolyte electroabsorption [spectroscopy]
EER	electrolyte electroreflectance [spectroscopy]
EIS	electrochemical impedance spectroscopy
EL	electroluminescence
ELS	electron loss spectroscopy
EMA	effective mass approximation
EMIRS	electrochemically modulated infrared spectroscopy
EQE	external quantum efficiency
ETA	extremely thin absorber
EUR	euro (1 EUR = 1 ECU $\approx$ US\$ 1.43)
EXAFS	X-ray absorption fine structure
fb	(as a superscript or subscript) flat band
FCWD	Franck-Condon weighted density of states
FRA	frequency response analyser

FTIR	Fourier transform infrared [spectroscopy]
FTO	fluorine-doped tin oxide
G	global (irradiance)
GC	gas chromatography
HOMO	highest occupied molecular orbital
HRELS	high-resolution electron loss spectroscopy
ILGAR	ion layer gas reaction
IMPS	intensity-modulated photocurrent spectroscopy
IPCE	incident photon to current conversion efficiency
IPET	interparticle electron transfer
IMVS	intensity-modulated photovoltage spectroscopy
IQE	internal quantum efficiency
ISS	ion scattering spectroscopy
LC	liquid chromatography
Lt	(as a superscript or subscript) in the light
LED	light-emitting diode
LEED	low-energy electron diffraction
LMMRS	light-modulated microwave reflectance spectroscopy
LPE	liquid phase epitaxy
LUMO	lowest unoccupied molecular orbital
MBE	molecular beam epitaxy
MEG	multiple exciton generation
MG	metallurgical grade
MIS	metal/insulator/semiconductor (junction or device)
MOCVD	metallo-organic chemical vapour deposition
mp	(as a superscript or subscript) maximum power
MS	mass spectrometry
MS	metal/semiconductor (junction or device)
oc	(as a superscript or subscript) open circuit
Ox	oxidant
P3HT	poly(3-hexylthiophene)
PAH	polyaromatic hydrocarbon
PCBM	[6,6]-phenyl C ₆₁ -butyric acid methyl ester
PEIS	photoelectrochemical impedance spectroscopy
PL	photoluminescence
POM	polyoxometallates
PMC	photoinduced microwave conductivity

PPV	poly(<i>para</i> -phenylenevinylene)
PV	photovoltaic
pzc	potential of zero charge
QD	quantum dot
QNR	quasi-neutral region
QY	quantum yield
Rd	reductant
RIP	radical ion pair
rms	root-mean square
RSC	regenerative solar cell
SC	solar cell
sc	(as a superscript or subscript) short circuit
SCE	saturated calomel electrode
sc1	(as a superscript or subscript)
SHE	standard hydrogen electrode
SILAR	successive ion layer adsorption
SNIFTIRS	subtractively normalised interfacial Fourier transform infrared spectroscopy
SIMS	secondary ion mass spectrometry
SIS	semiconductor/insulator/semiconductor junction
ss	(as a superscript or subscript) surface state
STC	Standard Test Conditions
TCE	trichlorethylene
TCO	transparent conducting oxide
TEM	transmission electron microscopy
TOC	total organic carbon
TOF	turnover frequency
TON	turnover number
TOR	turnover rate
TRMR	time-resolved microwave reflectivity
UPS	ultraviolet photoelectron spectroscopy
vb	(as a subscript or superscript) valence band
VOC	volatile organic compound
W _p	peak watts
XPS	X-ray photoelectron spectroscopy

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